

Complex Formation and Stereoselective Effects in the
Copper(II) d- and dl-Tartrate Systems in Acid and
Neutral Aqueous Solution

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Abstract

The complex formation in aqueous solution between copper(II) ion and tartaric acid in the d- and dl-forms (d-tartrate = R,R-tartrate) has been studied in the acid and neutral pH-range at 25°C. A potentiometric method with the use of glass- and copper amalgam electrodes has been applied. A formal ionic strength equal to one mol·dm⁻³ was maintained by the addition of sodium perchlorate.

Experimental data were analysed as to the complexes formed and their stability constants. At pH < 4 both of the systems are characterized by an equilibrium between mononuclear and binuclear species, CuTH, CuT₂ and Cu₂T₂ and Cu₂T₂H₋₁ respectively (T = C₄H₄O₆²⁻). At increasing pH up to neutrality the hydrolysis of the dimers continues to Cu₂T₂H₋₂ but at the same time an additional condensation takes place.

From a comparison of the stability constants of the complexes in the two systems it is concluded that the dd- and ll-enantiomers of Cu₂T₂ are stereospecifically formed in the copper dl-tartrate system. In the case of Cu₂T₂H₋₁ and Cu₂T₂H₋₂ the formation of the enantiomers is still favoured but increasing amounts of dl-isomers are formed. The ratio between the amounts of the enantiomeric species and the dl-isomer of CuT₂ is close to that statistically expected if structural effects are absent.

Some differences in the formation of the polynuclear complexes at pH > 4 are discerned. The predominating complex in neutral

solutions has in both of the systems studied the stoichiometric formula $\text{Cu}_4\text{T}_3\text{H}_{-5}$ but is in the d-tartrate system best represented by $\text{Cu}_8\text{T}_6\text{H}_{-10}$ while for the description of the dl-tartrate system only $\text{Cu}_4\text{T}_3\text{H}_{-5}$ is needed.

Introduction

There are several reports on stereoselective effects in the complex formation between the copper(II) ion and optically active and racemic tartrate [1]. Copper(II) d-tartrate and copper(II) dl-tartrate in alkaline solutions exhibit colour differences that are discernable with the naked eye. ESR spectra from solutions of the latter kind have been interpreted on the basis of the predominance of a dimeric unit [2,3], $[\text{Cu}_2\text{d-TH}_{-2}\text{l-TH}_{-2}]^{4-}$. This unit has also been identified in an X-ray study [4] of $\text{Na}_2\text{Cu}\text{dl-C}_4\text{H}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$. The absence of the corresponding $\text{Cu}_2(\text{d-TH}_{-2})_2$ or $\text{Cu}_2(\text{l-TH}_{-2})_2$ dimers is supported by the fact that ESR-spectra of alkaline copper d-tartrate reveal no dimeric units [2] and that attempts to precipitate the corresponding solid phase from alkaline copper(II) d-tartrate solutions give substances with variable compositions [4]. These observations are in accordance with the prediction by Tapscott et al. in their review on tartrate-bridged binuclear complexes [5], that the dl-isomer is more stable than corresponding dd- and ll- isomers if the coordination geometry is tetragonal.

It is well established that weakly acid copper(II) tartrate solutions contain binuclear complexes as well [6-9]. However,

absorption [1] and ESR [2] spectra of acid copper(II) d- and dl-tartrate solutions do not differ. This would indicate that only dd- and ll-dimers are formed in the acid copper dl-tartrate solution. Yet, the possibility of dl-isomers with spectral characteristics identical with the dd- and ll-isomers remains.

A determination of the stability constants of the complexes present in acid copper(II) d- and dl-tartrate solutions under exactly the same experimental conditions could give a definite answer to the question of stereoselectivity of the complex formation in these solutions. A great many equilibrium studies of the copper(II) tartrate system have been performed but only two of them form a basis for a direct comparison between the two systems. Fronaeus [10] determined from potentiometric measurements the stability constants of the mononuclear complexes and found a difference in the values of the stability constants of the first complex, CuT . Such a difference is not expected but must reflect any other divergent behaviour of the two systems. Simeon et al. [11] who used a polarographic method, described their measurements with only one complex, the 1:1 complex, and found no difference in the complex formation between the d- and dl-tartrate systems in the pH-range 2-5.

Another region of interest is the pH-range 5-8. At pH about 4 a further polymerisation beyond the binuclear complexes begins and results in a large pH jump when 1.25 mol OH^- /mol

Cu(II) is added [12]. Again, no differences between d- and dl-tartrate may be discerned either from ESR [13] spectra or from magnetic susceptibility [13] measurements. From neutral copper(II) d- and dl-tartrate solutions solid phases containing the stoichiometric unit $\text{Cu}_4\text{T}_3\text{H}_{-5}^{3-}$ have been prepared [14-16]. However, there is a remarkable difference between the copper d- and dl-tartrate solution as to the solubility of these solids [14].

In the present work the complex formation between the copper(II) ion and d-tartrate as well as dl-tartrate has been studied under the same experimental conditions. The concentrations of the free ions Cu^{2+} and H^+ have been determined simultaneously by a titration procedure using copper amalgam and glass electrodes. The solutions were made from copper(II) perchlorate, tartaric acids, and sodium hydroxide and with an ionic medium of sodium perchlorate creating a formal ionic strength equal to one $\text{mol}\cdot\text{dm}^{-3}$. The study was limited to the acid and neutral pH-range, a region of reliable behaviour of the amalgam electrode.

Method of calculation

With T representing the tartrate ion, $\text{C}_4\text{H}_4\text{O}_6^{2-}$, a copper(II) tartrate complex may be written $[\text{Cu}_p\text{T}_q\text{H}_r]^{2(p-q)+r}$. In the following the charges will generally be omitted. r will take both positive and negative values, a negative value means that protons have been lost or hydroxide ions coordinated. If the free concentrations of the copper(II), tartrate and



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hydrogen ions are represented by m , t , and h the stability constant is defined by

$$\beta_{pqr} = \frac{C_{pqr}}{m^p t^q h^r} \quad (1)$$

Assuming constant activity factors the β_{pqr} 's are real constants and for the total concentrations of each point of measurement the following equations are valid

$$C_M = m + \sum_{p=1} \sum_{q=0} \sum_r p \beta_{pqr} m^p t^q h^r \quad (2)$$

$$C_T = t + \sum_{p=0} \sum_{q=1} \sum_r q \beta_{pqr} m^p t^q h^r \quad (3)$$

$$C_H = h - oh + \sum_{p=0} \sum_{q=0} \sum_r r \beta_{pqr} m^p t^q h^r. \quad (4)$$

To each set of total concentrations there are two simultaneously measured electromotive forces (emfs), whose values in mV units are related to corresponding free concentrations by

$$E_m = E_m^O - S_m \ln m + E_j \quad (5)$$

and

$$E_h = E_h^O - S_h \ln h + E_j. \quad (6)$$

E_j is a correction term which is supposed to have approximatively the same value in the two expressions [17]. Its meaning will be discussed later.

The calculation of the stability constants is entirely done

by means of a numerical method in which the least square function

$$S = V^T M_f^{-1} V \quad (7)$$

is minimized. V is the vector of emf residuals and M_f the moment matrix. In order to avoid too extensive calculations all correlation coefficients of M are neglected except those between E_m and E_h of the same point of measuring. The sum will then reduce to

$$S = \sum_i [w_{m,i} (E_{m,i}^{\text{exp}} - E_{m,i}^{\text{cal}})^2 + w_{h,i} (E_{h,i}^{\text{exp}} - E_{h,i}^{\text{cal}})^2 - w_{mh,i} (E_{m,i}^{\text{exp}} - E_{m,i}^{\text{cal}}) (E_{h,i}^{\text{exp}} - E_{h,i}^{\text{cal}})] \quad (8)$$

Weighing. The weights in Eq. 8 are given by

$$w_{m,i} = \frac{c}{\text{var}(E_{m,i}) (1 - \rho_{mh,i}^2)} \quad (9)$$

$$w_{h,i} = \frac{c}{\text{var}(E_{h,i}) (1 - \rho_{mh,i}^2)} \quad (10)$$

$$w_{mh,i} = \frac{2 c \rho_{mh,i}}{[\text{var}(E_{m,i}) \cdot \text{var}(E_{h,i})]^{1/2} (1 - \rho_{mh,i}^2)} \quad (11)$$

where c is an arbitrary constant and $\rho_{mh,i}$ the correlation coefficient ($\rho_{mh,i} = \text{cov}(E_{m,i}, E_{h,i}) / [\text{var}(E_{m,i}) \cdot \text{var}(E_{h,i})]^{1/2}$).

It is difficult to assign adequate values to the moments - especially the covariance - directly from the experimental emf data, so they are estimated from an analysis of the origins of the errors. The measured emf is a function of independent, experimentally controlled variables, x_n (such as stoichiometric concentrations and volumes), to which a term, ε , is added accounting for the error of the mere measurement of the emf and independent of the x_n 's,

$$E_i = f(x_{1,i}, x_{2,i}, \dots, x_{N,i}) + \varepsilon_i. \quad (12)$$

Some of the variables x_n may cause a considerable correlation between E_m and E_h , especially in the area $C_H/C_M < 0$. The functional relationship between E and the x_n variables are taken from Eqs. 2-6 and pertinent volumetric relations. Since the variables are at large statistically independent the expressions of the sought moments can be simplified to

$$\text{var}(E_i) = \text{var}(\varepsilon_i) + \sum_n \left(\frac{\partial E}{\partial x_n} \right)_i^2 \text{var}(x_{n,i}) \quad (13)$$

and

$$\text{cov}(E_{m,i}, E_{h,i}) = \sum_n \left(\frac{\partial E_m}{\partial x_n} \right)_i \left(\frac{\partial E_h}{\partial x_n} \right)_i \text{var}(x_{n,i}). \quad (14)$$

As independent variables of importance in Eqs. 13 and 14 the following have been selected; the stoichiometric concentrations of the titrand and titrator solutions, the concentration of protolytic impurities of the ionic medium, the separately determined protolysis constants of the tartaric acid, the start and addition volumes of titration and finally the variables

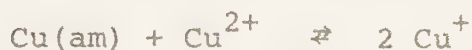
ϵ_m and ϵ_h . However, the variances of all these variables are not known either but have been assigned values by means of an estimation of the maximum errors. Any variation of the temperature has been neglected. The errors in E^0 are included in the estimation of $\text{var}(\epsilon_i)$.

As mentioned above the correlation between emfs of different points of measuring was disregarded. Some of the enumerated experimental variables contribute more or less to such a correlation. The sodium hydroxide concentration of the titrator solution is the most fatal in this sense. For this reason the sodium hydroxide concentration of each titrator solution is treated as an unknown quantity.

The parameters to be varied in order to find a minimum of the function S in Eq. 8 are thus the stability constants β_{pqr} , except β_{011} and β_{012} , and a number of concentration variables one for the sodium hydroxide concentration of each titration series. As the complete model for the complex formation is not known, all plausible sets of species have to be tried. For the minimization process the FORTRAN subroutine STEPIT [18] has been used, completed with routines for the necessary fitting of data for STEPIT and for the calculation of the function S . The weights are calculated by evaluating the derivatives of Eqs. 13 and 14 analytically from the mathematical expressions. As this is a rather time-consuming process, the weights are calculated with the start values of the parameters and then retained throughout the run. Restarting the run and recalculating the weights from the new set of parameters makes

it possible to check that the set of weights is consistent with the final values of the parameters. In order to avoid an ungainly large number of unknown parameters the E° -values are determined separately, but when an acceptable set of parameters has been found the E° -values have been varied alone in order to reveal any discrepancies in their values.

The calculation of the total concentrations requires that a few corrections are made. As the total concentration of copper(II) in some series is rather low, the effect of the disproportionation reaction



has been corrected for by subtracting an amount of $\sqrt{Km}/2 \text{ mol} \cdot \text{dm}^{-3}$. For the equilibrium constant, K , the value of $10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ is used [10]. The complex formation between Cu(I) and the tartrate ion has been neglected as it is supposed that it is much inferior to that of Cu(II) in coordinating an oxygen donor ligand such as the tartrate ion.

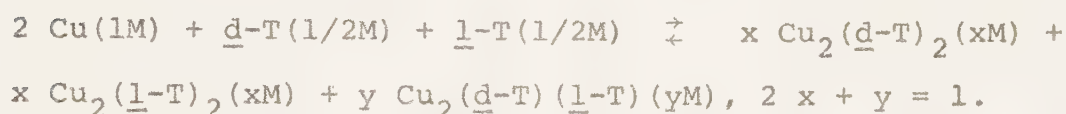
For the entire concentration region used the copper(II) concentration is low enough and the formation of tartrate complexes sufficiently strong so that hydrolysis of the copper(II) ion [19] can be neglected.

The correction term E_j in Eqs. 5 and 6 represents the deviation from a constant value E° which may be the result of liquid junctions or media effects. Irrespective of the origins of

the effects it is reasonable to suppose that any departure from the pure ionic medium of one molar sodium perchlorate will contribute more or less to E_j . In this work E_j is hypothetically considered as a sum of contributions from each kind of electrolyte that makes up the complex solution. As a linear relationship is often found within wide concentration ranges between E_j and the concentration of a species that replaces the inert salt [20,21], E_j is approximated as a sum of linear terms. The sum includes a term accounting for the deviation of the sodium perchlorate concentration itself from one $\text{mol}\cdot\text{dm}^{-3}$. Only species with high concentration are expected to give marked contributions to E_j . As the copper concentration is not very high the concentrations of the complexes are low and their contributions to E_j may be disregarded. The linear coefficients of the correction terms of the other electrolytes that are present in the complex solution, may be determined separately.

A complex $\text{Cu}_p\text{T}_q\text{H}_r$ in the copper(II) dl-tartrate system is either a pure d-tartrate complex formed together with the analogue l-enantiomer of if $q \geq 2$ a complex with both d- and l-tartrate ligands, here named a dl-complex. The two kinds of complexes may exist together in the dl-tartrate system and each species with the formula $\text{Cu}_p\text{T}_q\text{H}_r$ will contribute to the experimentally determined stability constant. The formation of dl-complexes is revealed in a comparison of this stability constant with the corresponding one of the copper(II) d-tartrate system. However, in such a comparison it must be

kept in mind, that, since the racemic system is treated as a one-ligand system in the calculations according to the description above, the compared constants do not refer to the same standard state as for the free ligand and the complexes formed. If we take the complex Cu_2T_2 as an example, the constant β_{22} determined from calculations on the racemic system will represent the free energy change of the reaction



Let us denote with $\beta_{pq}^{q-n,n}$ the stability constant of the complex $\text{Cu}_p(\underline{\text{d}}\text{-T})_{q-n}(\underline{\text{l}}\text{-T})_n$, which represents the free energy change in the normal standard state e.g.



The relations between a constant β_{pq} of the dl-system calculated in the way described and the number of $\beta_{pq}^{q-n,n}$ constants are then easily shown to be

$$\beta_{pq} = \sum_{n=0}^{\frac{q-1}{2}} (1/2)^{q-1} \beta_{pq}^{q-n,n}, \quad q \text{ odd} \quad (15)$$

and

$$\beta_{pq} = (1/2)^q \beta_{pq}^{\frac{q}{2}, \frac{q}{2}} + \sum_{n=0}^{\frac{q}{2}-1} (1/2)^{q-1} \beta_{pq}^{q-n,n}, \quad q \text{ even.} \quad (16)$$

The upper limit of summation is explained by the identity between $\beta_{pq}^{q-n,n}$ and $\beta_{pq}^{n,q-n}$.

$\beta_{pq}^{q,0}$ is obtained from the measurements on the copper(II) d-tartrate system. Thus, for complexes with $q \leq 3$ the individual $\beta_{pq}^{q-n,n}$ values can be calculated from Eqs. 15 or 16 and can be used for a direct comparison. Hence it is seen that the formation of dl-complexes implies for the β_{pq} constant of the dl-system that $\beta_{pq} > 2^{\frac{1}{q}-1} \beta_{pq}^{q,0}$.

The formation of a dl-complex is statistically favoured [22]. When comparing the constants in order to search for stereo-selective effects of structural origins the $\beta_{pq}^{q-n,n}$ value should be divided by a statistical factor, $R = \binom{q}{n}$ [23].

Experimental

Chemicals. Copper(II) perchlorate, $\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ (BDH), was recrystallized once. The prepared stock solution was analyzed for copper by electrolytical deposition. The amount of free acid was determined to be $2.04 \times 10^{-3} \text{ mol H}^+/\text{mol Cu}^{2+}$ by potentiometric titration.

The racemic tartaric acid, $\text{dl-C}_4\text{H}_6\text{O}_4 \cdot \text{H}_2\text{O}$ (Fluka, purum) was recrystallized three times (m.p. $202-204^\circ\text{C}$).

The optically active tartaric acid, $\text{d-C}_4\text{H}_6\text{O}_4$ (Merck p.a.) was used without further purification. The concentrations of the stock solutions of the two acids were determined by alkali-metric titration.

Sodium perchlorate was prepared by the neutralisation of perchlorate acid (Baker p.a.) with sodium carbonate (Merck p.a.) and sodium hydroxide to $\text{pH} = 7$. Precipitated impurities were

filtered off and the perchlorate was crystallized as $\text{NaClO}_4 \cdot \text{H}_2\text{O}$. The amount of protolytic impurities was analyzed potentiometrically in a 1.000 M solution. The protolyte present corresponds in total to $1.5 \times 10^{-5} \text{ M OH}^-$.

The preparation of the copper amalgam, ca 2%, has been described in Ref. 24.

Method. The emfs of the following two cells were measured at 25°C .

-	glass	$C_M \text{ Cu}(\text{ClO}_4)_2$			
-	electrode	$C_T \text{ H}_2\text{T}$	1 M	0.010 M NaCl	Ag, AgCl +
		$C_{OH} \text{ NaOH}$	NaClO_4	0.99 M NaClO_4	
-	Cu-Hg	$(1-3C_M - C_{OH})$			
		NaClO_4			

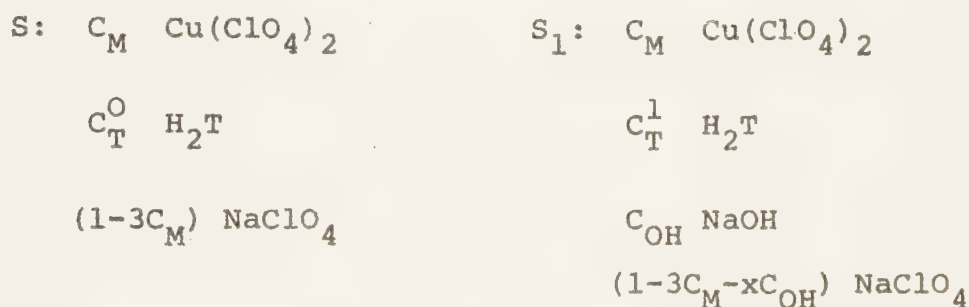
All other factors apart from the glass and amalgam electrode were the same for the two cells during the titration procedure. The glass electrode was a Jena U 9201 and its emf was read with a precision of $\pm 0.1 \text{ mV}$ from a Radiometer PHM 52 digital potentiometer. The slope of this measuring device, S_h in Eq. 6, was determined as 58.81 mV. Before and after each titration the glass electrode was checked in a buffer solution of constant pH.

The emf of the amalgam electrode cell was measured with a Norma potentiometer and by the use of a Kipp en Zonen Galvanometer as a zero instrument. The emf could be read with $\pm 0.01 \text{ mV}$ precision. For S_m in Eq. 5 the theoretical value 59.16 mV was used.

The emfs were usually stable after a few minutes, but a little slower response was discerned in the dl-system in the region of rapid change of pH.

The reference electrode was prepared according to Brown 25 .

The composition of the left half-cell solution was changed during the titration by adding an increasing volume of a solution S_1 to 20 ml of a start solution S_0 . The solutions S_0 and S_1 had the following compositions



In most of the series $C_T^O = C_T^1 \cdot x$ in the expression of the sodium perchlorate concentration of solution S_1 has normally been chosen equal to 1 but in a couple of series with high tartrate concentration the sodium perchlorate concentration is further reduced ($x = 1.47$).

Before the titration a stream of oxygen-free nitrogen, pre-moistened in a 1.00 M sodium perchlorate solution was passed through the solutions for half an hour. During the titration the same nitrogen stream was bubbled through the titration vessel.

The protolysis constants of the acids were determined under the same experimental conditions as above. The hydrogen ion

concentration was measured with the glass electrode in titration series with constant concentration of the acid and varying amounts of sodium hydroxide or perchloride acid.

Measurements and results

As to the concentration ranges the principal aim has been to study and compare the formation of binuclear complexes or any further condensation products in weakly acid or neutral solutions equimolar in copper(II) and tartrate or with a moderate excess of tartrate. The corresponding series divide into two groups, one with $C_M = C_T$ and the other with $C_T > C_M$. In each of this kind of series C_M and C_T are constant while pH is changed from 2.5 to about 7. In the case of dl-tartrate the ratio $C_H/C_M = -1.25$ is not reached because of the onset of precipitation which occurs even at low copper concentration (< 5 mM) in the sodium ion medium. Otherwise, the upper limit of C_M is set by the low solubility of the neutral copper tartrate. At unfavourable pH values the solutions are supersaturated even at low values of C_M but only at $C_M = 20$ mM does the onset of precipitation disturb the execution of the titration. As the formation of binuclear complexes begins at very low copper concentrations, series with C_M as low as 1 mM have been performed. The tartrate concentration in these two groups of series does not exceed 50 mM. In a couple of series with low copper(II) concentrations,

1 and 2 mM, C_T was varied up to about 100 mM at $\text{pH} \approx 4.5$ ($[\text{T}]/[\text{HT}] \approx 7$) with the intention of obtaining data for the characterization of the mononuclear complexes. Higher concentrations of tartrate have been avoided as an extreme substitution of perchlorate with the doubly charged tartrate ion will probably cause serious changes of the medium.

The titration data are given in Table 1 and 2. Fig. 1 shows two representative titration curves, one for each system. As earlier reported [16,26] both of the systems exhibit a large potential jump when C_H/C_M approaches -1.25.

Protolysis constants. For the measurement of the protolysis constants, titrations series with $C_T = 5, 10, 25$, and 50 mM and varying pH were performed. The constants were calculated numerically. The following constants were obtained,

$$\underline{\text{d-tartaric acid}} \quad K_{a_1} = (1.809 \pm 0.008) \times 10^{-3} \text{ (M)}$$

$$K_{a_2} = (2.043 \pm 0.009) \times 10^{-4} \text{ (M)}$$

$$\underline{\text{dl-tartaric acid}} \quad K_{a_1} = (1.807 \pm 0.007) \times 10^{-3} \text{ (M)}$$

$$K_{a_2} = (2.048 \pm 0.007) \times 10^{-4} \text{ (M)}$$

The constants are given with 99% confidence intervals. No significant divergence between the protolysis constants of the two acids is observed. No indication of association between d- and l-tartrate ions of the racemic acid could be detected in the examined concentration region.

Emf-corrections. When determining E_m^O of the copper amalgam electrode it was observed that E_m^O varied linearly with the copper(II) concentration in the examined range up to 100 mM. The slope of the variation depends, however, on the way the ionic medium is maintained. The slopes are -26.9, -15.8, and -6.9 mV·M⁻¹ respectively when $([Cu^{2+}] + [Na^+]) = 1\text{ M}$, $[ClO_4^-] = 1\text{ M}$, and finally the formal ionic strength $I = 1\text{ M}$. These observations are consistent with the hypothesis of E_j as a sum of linear terms and make it possible to calculate the linear emf correction coefficients of copper and sodium perchlorate. The emf correction coefficients of the tartrate species were obtained from three titration series on different tartrate buffers. In each series the total concentration of tartaric acid was varied but the ratio C_{OH}/C_{H_2T} was kept constant (0.33, 1.00, and 1.67) as was the ionic strength. The correction coefficients were calculated from the titration data assuming that the protolysis constants are real constants throughout the titration range.

The separately determined emf correction coefficients are summarized below.

NaClO ₄	Cu(ClO ₄) ₂	HClO ₄	Na ₂ T	NaHT	H ₂ T	
-9	-34	49	11	-3	-13	mV·M ⁻¹

The emf correction amounts at most to 3.6 mV. The greatest part of this derives from the often rather large deviation of the sodium perchlorate concentration from one mol·dm⁻³ but the influence of high tartrate(2-) concentrations may

also be important in some titration series. An attempt to estimate the contribution to the emf correction from the complexes by guessing reasonable values of their correction coefficients showed that this contribution should be very modest (≈ 0.1 mV).

An inspection of the data obtained does not readily reveal what complexes are formed except that in the area of the potential jump there should appear complexes that are at least tetranuclear. In order to find a model to describe the data, the existence of a large number of complexes has to be tested. As the presence of coexisting complexes, including polynuclear as well as hydrolysed species, is expected, the difficulty in finding a unique model significantly better than all others, must be recognized. Complexes with a low overall concentration are especially hard to identify correctly, or systematic errors may even be interpreted as such complexes. As a consequence, complexes which appear in the calculations with a presence less than 10 - 15% relative to the total copper concentration, have been omitted from the final sets of complexes. Otherwise the effect on the sum of S in eq. 8 and the magnitude of the variances have been the criteria in deciding to adopt or omit a given complex.

In the final calculation of the constants and their variances the series with $C_M = 20$ mM have been omitted. As mentioned above the precipitation of copper tartrate began to interfere in these series. The calculations of the d-tartrate

system show discrepancies in the most critical pH-range of these series that cannot be eliminated by the introduction of a new complex. For the sake of uniformity the 20 mM series of the dl-tartrate system were omitted too in the final calculation, but in this case the obtained constants describe the data of these series quite well.

When $C_H/C_M \geq 0$ corresponding to a pH lower than 4.0-4.5 the systems can be described with mono- and binuclear complexes, mainly $CuTH$, CuT and Cu_2T_2 . At this low pH there is, however, a considerable hydrolysis of the binuclear complex Cu_2T_2 into $Cu_2T_2H_{-1}$ and even $Cu_2T_2H_{-2}$. The calculations give no evidence that complexes more condensed than the binuclear are formed in this area.

When the pH is increased the hydrolysis of the binuclear complexes continues but soon the formation of more condensed species becomes predominant. The hydrolysis of CuT into $CuTH_{-1}$ in this pH-range [27] cannot be traced. When C_H/C_M approaches -1.25 the pH increases rapidly to about 8 and at the same time $[Cu^{2+}]$ is reduced in a corresponding way indicating an almost quantitative formation of complexes with the ratio of Cu:H equal to 1:-1.25. The calculations give the best fit to the experimental data if the species formed up to this equivalence point have the stoichiometric relation Cu:T:H equal to 4:3:-5. A close examination of the area of the pH jump -without sodium perchlorate- showed that in the case of dl-tartrate the change of pH is less than in the case of d-tartrate and that the titration curve

is not quite so steep. Small amounts of more hydrolysed complexes are obviously formed in the dl-system and the formation of the 4:3:-5 complex is not completely quantitative.

The 4:3:-5 complex is earlier reported as $\text{Cu}_4\text{T}_3\text{H}_{-5}$ [28] or $\text{Cu}_8\text{T}_6\text{H}_{-10}$ [29]. The potentiometric data of this study give some indication of both of these complexes being present in the d-tartrate system while the introduction of an trimer, $\text{Cu}_{12}\text{T}_9\text{H}_{-15}$ brings no improvement. Recordings of absorption and circular dichroism spectra [30] of copper d-tartrate solutions with $C_{\text{H}}/C_{\text{M}} = -1.25$ and C_{M} varying from 2 to 100 mM show, however, that Beer's law is perfectly obeyed which is a strong indication that only one complex is present. The best fitting of data is then obtained if $\text{Cu}_8\text{T}_6\text{H}_{-10}$ is applied and if the formation of this complex is preceded by another, less hydrolysed, complex viz. $\text{Cu}_6\text{T}_4\text{H}_{-7}$. The formation of an octanuclear complex is supported by the results of an X-ray investigation on a concentrated copper d-tartrate solution [30].

For the description of the dl-tartrate system only a tetranuclear 4:3:-5 complex is required, but also in this case there are indications of appreciable amounts of some other species in the range $-1.25 < C_{\text{H}}/C_{\text{M}} < -1.00$. This species is best characterized as $\text{Cu}_6\text{T}_5\text{H}_{-7}$, but it must be pointed out that complexes with a similar stoichiometric composition may fit almost as well.

In earlier works the existence of the complex Cu_2T_3 has been claimed [7,9]. The reported stability constants are assigned values large enough for the complex to be present in the solutions with excess of tartrare. The preliminary calculations do not exclude the existence of this species, but its calculated stability constant has very low statistical significance and its presence is not needed for the description of data. The same may be said of the complex CuT_3 which would possibly appear at high values of C_T in the series with varying C_T .

In all about 75 complexes have been tested. Table 3 shows the complexes which were finally chosen to describe the complex formation in the acid and neutral region of the copper(II) d- and dl-tartrate systems. The two sets of complexes describe corresponding systems with practically the same degree of precision. Where relevant, stability constants of single dl-complexes calculated according to Eqs. 15 or 16 are given in Table 3.

It may be noted that the values of some constants are rather sensitive to changes of the model of description and may be somewhat more uncertain than would be inferred from the stated errors. As might be expected some constants show a large correlation, e.g. $\rho_{110,220}$ is equal to -0.87 in the d-tartrate system and -0.74 in the dl-system.

Discussion

Complexes and corresponding stability constants of the present work are in particular instances in good agreement with some earlier investigations. However, different authors have examined the complex formation in different concentration ranges and thus consider different sets of complexes.

The view of the systems as mainly built up by CuT and Cu_2T_2 in acid and equimolar solutions [6-8] is confirmed in this work. The absence of more condensed species in this pH range has been shown to be valid in an increased concentration area up to the limit set by the solubility of the copper tartrate. The stability constants of the complexes CuT and Cu_2T_2 show small differences from the corresponding values of Bottari et al. [7]. As should be expected the values of the stability constants obtained for the complexes CuTH and CuT do not differ significantly between the two systems. The magnitude of β_{111} is surprising as it implies that the neutral species CuT is as strong a base -or even stronger- as the negatively charged hydrogen tartrate ion HT^- (CuT : $k = 900$; HT^- : $k = 560 \text{ (M}^{-1}\text{)}$, $k = k_p/k_w$).

As soon as a complex contains more than one tartrate group there are possibilities for the formation of diastereomers of this complex in the dl-tartrate system. When discussing the origins of any stereoselectivity in solution, the experiences from the coordination of the tartrate ion obtained from a large number of crystal structure determinations of metal tartrates [5,31] are valuable. When chelates are

formed a five-membered ring is created by the use of adjacent carboxyl and hydroxyl oxygens as donors. It is also observed that the staggered conformation (Fig. 2) of the tartrate ion with the carboxyl groups opposite each other is retained and not very much changed when the tartrate ion is coordinated (Fig. 2).

The stability constant of the dl-complex $\text{Cu}(\underline{\text{d-T}})(\underline{\text{l-T}})$ is about twice as large as that of $\text{Cu}(\underline{\text{d-T}})_2$. Recognizing the statistical factor $R = 2$ for this complex it turns out that the greater stability of the dl-complex is of statistical origin. If planar complexes with chelates of the kind mentioned are assumed, the negatively charged carboxyl oxygens will probably be placed in trans position. The complexes $\text{Cu}(\underline{\text{d-T}})(\underline{\text{l-T}})$ and $\text{Cu}(\underline{\text{d-T}})_2$ or $\text{Cu}(\underline{\text{l-T}})_2$ will then differ by the fact that the former places the non-coordinated tartrate moieties at each side and the latter at the same side of the coordination plane. If so, the absence of stereoselectivity indicates that the non-coordinated carboxyl groups of the $\text{Cu}(\underline{\text{d-T}})_2$ complex do not interact or take part in the coordination to any greater extent. A study of molecular models shows that they may be kept at a satisfactory distance from each other without violating the conformation of the tartrate ligand.

The stability constants of the Cu_2T_2 complex show that the formation of this complex in dl-tartrate solutions is practically stereospecific in favour of pure d- and l-complexes. A stereoselectivity of the same sort has been

deduced for the corresponding nickel tartrate complex, Ni_2T_2 , from pressure-jump kinetic studies by Hoffman et al. [32,33].

In the case of $\text{Cu}_2\text{T}_2\text{H}_{-1}$ and $\text{Cu}_2\text{T}_2\text{H}_{-2}$ the calculated constants indicate that dl-complexes are formed but that the dd- and ll-complexes are still favoured. $\text{Cu}_2\text{T}_2\text{H}_{-1}$, and -to a greater extent- $\text{Cu}_2\text{T}_2\text{H}_{-2}$, are formed in the region where the continued polymerisation takes place. It is difficult to exactly establish the most suitable model of the complex formation in this region. Due to inadequacies in the adopted models, the stability constants of these two complexes may be somewhat more uncertain than is suggested from the stated errors. However, the results of the testing of various models in the preliminary calculations do not call the existence of the dl-complex of $\text{Cu}_2\text{T}_2\text{H}_{-2}$ in question whereas the existence of the corresponding $\text{Cu}_2\text{T}_2\text{H}_{-1}$ complex is more uncertain.

The tartrate-bridged binuclear structures, the occurrence of which has been established for many crystal structures [4,5,31] of metal tartrates, and which are evidently present in some alkaline metal tartrate solutions [2,34], have also been used in the discussion of the binuclear tartrate complexes formed in acid solution [9,33].

In an assessment of the conformation angles and the strain induced in the central carbon-carbon bond of the tartrate ions when a tartrate-bridged binuclear complex is formed,

Tapscott [35] has shown that the tetragonal coordination geometry with a square planar arrangement of the chelate rings is most favourable for a dl-complex (Fig. 3). A dd- or ll-complex with tetragonal geometry should imply a somewhat higher conformational energy [36] -ca. $5 \text{ kJ}\cdot\text{mol}^{-1}$ - than that of the dl-complex. However, the conformational energy is lowered if the coordinative bonds to the trans-positioned hydroxyl oxygens form an angle less than 180° . A minimum of the conformational energy would be reached when the chelate rings are arranged in a manner somewhere between a trigonal bipyramidal (Fig. 3b) and octahedral geometry (Fig. 3c). At the same time configuration isomerism is introduced into the binuclear structure. The steric possible configurations are $\Delta\Delta(\underline{dd})$ and $\Lambda\Lambda(\underline{ll})$ [35].

The tetragonal geometry is represented by the dimer $[\text{Cu}_2\underline{d}\text{-TH}_{-2}\underline{l}\text{-TH}_{-2}]^{4-}$ mentioned in the introduction. In this complex the carboxyl oxygens occupy cis positions. These negatively charged oxygens are balanced by the likewise negatively charged deprotonated hydroxyl oxygens on the other side of the central ion. When the hydroxyl protons are retained, as in the Cu_2T_2 complex formed in acid solution, the cis position of the repelling carboxyl oxygens in a dl-complex should be unfavourable. The possibility of a trans position is offered by the formation of the enantiomeric dd- and ll-complexes.

According to the above the chelate rings in the dd- and ll-complexes should form an angle less than 180° to each other.

An almost perfect octahedral geometry is found in the dimeric copper tartrate unit in the crystal structure of $\text{Cu}_2\text{d}-\text{C}_4\text{H}_4\text{O}_6 \cdot 3 \text{H}_2\text{O}$ [31]. However, the geometries of the complexes in solution may be different. The circular dichroism spectra of the dd-complexes Cu_2T_2 and $\text{Cu}_2\text{T}_2\text{H}_{-1}$ differ markedly from that of $\text{Cu}_2\text{T}_2\text{H}_{-2}$ indicating a structural change when two hydroxyl protons are released [9,37]. In the $\Delta\Delta(\underline{\text{dd}})$ - or $\Lambda\Lambda(\underline{\text{ll}})$ -structures there may be a possibility for the formation of two intramolecular hydrogen bonds between hydroxyl oxygens of the opposite tartrate groups if the angle between the chelate rings is not too large. The strength of these hydrogen bonds ought to increase if protons are released. Possibly the loss of two protons is followed by a considerable decrease of the angle between the chelate rings. Then the Cu_2T_2 and $\text{Cu}_2\text{T}_2\text{H}_{-1}$ dd-complexes would represent a "wide-angled" geometry, for instance a trigonal bipyramidal as in Fig. 3b or even a distorted tetragonal geometry, while the dd-complex of $\text{Cu}_2\text{T}_2\text{H}_{-2}$ would approach an octahedral geometry (Fig. 3c).

The existence of the dl-complexes suggests that the disadvantage of cis-positioned carboxyl oxygens of the dl-structure is partly overcome when at least two hydroxyl protons are dissociated leading to an equilibrium between the diastereomeric tetragonal dl-complex and octahedral dd- and ll-enantiomers.

Although ESR- [13] and absorption [1] spectra of copper d- and dl-tartrate solutions in the neutral pH-range do not

differ, the present investigation indicates that there are differences in the complex formation in this region. The formation of complexes containing a number of copper ions that is a multiple of four in both of the systems is obvious from the titration curves (Fig. 1). If an octanuclear complex is formed in the d-tartrate solution the appearance of the d- and l-enantiomers of this complex would be expected in the dl-system too. However, at the relatively low concentrations that are accessible for measurements in sodium perchlorate medium the statistically unfavourable formation of the octanuclear enantiomers is easily suppressed by the stable and less condensed tetranuclear dl-complex.

In contrast to the copper dl-tartrate solution with $C_H/C_M = -1.25$ a corresponding d-tartrate solution can be made very concentrated. Such a solution ($C_M = 1.75$ M) has been subject to a large-angle X-ray investigation [30]. The introduction of the octanuclear complex in the d-tartrate system is consistent with the interpretation of the data from that investigation. $Cu_8T_6H_{-10}$ is represented in that work as the product of three dimers being linked via the hydroxyl oxygens by two copper ions. All hydroxyl protons are lost except one on each of the outer dimers. It is worth noting that the hydrolysed dimer $Cu_2T_2H_{-2}$ is present in the region of polymerisation and that the complex $Cu_6T_4H_{-7}$ could be suggested as an intermediate which will form the octanuclear complex upon the addition of another dimer.

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Table 1a. Experimental series data. Copper d-tartrate system

$$(C_H^O = 2 C_T^O ; C_H^1 = 2 C_T^1 - C_{OH})$$

Series	C_M	C_T^O	C_T^1	C_H^O	C_H^1	E_m^O	E_h^O
no	/mM	/mM	/mM	/mM	/mM	/mV	/mV
1	1.01	1.00		2.00	-2.98	16.60	527.8
2	2.02	2.00		4.00	-6.02	16.60	527.6
3	5.05	5.00		10.00	-14.87	16.25	528.0
4	10.10	10.00		20.00	-29.9	16.25	528.0
5	20.20	20.00		40.0	-60.4	16.65	528.5
6	2.02	10.00		20.00	-20.12	16.40	528.4
7	5.05	10.00		20.00	-20.01	16.40	528.3
8	2.02	25.0		50.0	-50.7	16.45	528.4
9	5.05	25.0		50.0	-50.0	16.40	528.4
10	10.10	25.0		50.0	-49.5	16.35	528.2
11	20.20	50.0		-49.7	100.0	16.25	528.0
12	1.01	0.00	160.0	0.00	19.9	16.35	528.2
13	2.02	0.00	160.0	0.00	19.7	16.35	528.2

Table 1b. Experimental point data. Copper d-tartrate system.

v /ml	E _m /mV	E _h /mV	v /ml	E _m /mV	E _h /mV	v /ml	E _m /mV	E _h /mV
Series no 1			Series no 5					
2.00	106.89	717.0	0.00	70.32	649.5	16.00	132.77	768.1
6.00	108.12	737.9	5.00	76.45	680.0	20.00	141.36	798.4
10.00	109.89	764.2	10.00	85.09	712.3	23.00	153.66	825.9
14.00	112.54	797.0	12.00	89.60	732.3	25.00	176.84	865.5
18.00	116.10	815.1	16.00	97.31	770.3	Series no 10		
22.00	120.24	826.5	20.00	103.22	782.9	2.00	83.72	666.8
26.00	125.35	838.2	24.00	109.67	792.3	5.00	91.30	685.8
30.00	132.46	852.4	28.00	117.97	803.1	7.00	97.20	698.0
34.00	145.08	874.9	32.00	125.56	818.7	9.00	103.27	710.6
36.00	159.07	897.6				12.00	111.69	729.9
Series no 2			Series no 6			16.00	120.30	755.5
2.00	98.80	704.4	0.00	99.93	670.4	20.00	127.17	780.2
6.00	100.93	726.2	2.00	102.95	684.7	24.00	134.28	799.9
10.00	103.73	752.8	4.00	105.82	697.9	28.00	143.58	817.5
14.00	107.03	784.6	6.00	109.99	710.3	31.00	155.96	838.0
19.00	110.64	802.1	8.00	114.22	722.1	33.00	177.88	873.5
22.00	114.72	812.9	10.00	118.19	733.8	Series no 11		
26.00	119.78	823.6	12.00	121.75	745.5	5.00	156.90	831.0
30.00	127.00	837.6	16.00	128.12	770.5	8.00	137.80	796.4
34.00	140.82	861.5	20.00	136.32	801.6	12.00	128.00	765.8
36.00	158.59	890.1	24.00	157.75	845.4	16.00	121.35	743.5
Series no 3			Series no 7			20.00	116.05	727.8
0.00	86.68	677.2	1.00	88.71	673.8	24.00	111.22	715.9
2.00	87.95	688.7	3.00	91.85	685.2	30.00	104.93	702.7
4.00	89.57	699.7	5.00	93.89	695.5	36.00	99.73	693.1
6.00	91.45	710.6	7.00	97.09	705.5	40.00	96.83	688.2
8.00	93.57	722.5	9.00	100.50	715.7	Series no 12		
10.00	95.84	736.4	12.00	105.75	731.8	0.20	114.53	779.5
12.00	98.16	753.0	16.00	112.20	755.1	0.60	127.77	783.6
16.00	102.27	781.9	20.00	117.87	778.6	1.00	135.26	786.8
20.00	106.18	794.2	24.00	123.47	796.1	1.50	141.26	789.2
24.00	110.56	803.3	28.00	129.78	809.3	2.50	148.81	791.7
28.00	116.11	813.2	32.00	138.59	824.3	4.00	155.36	793.5
32.00	124.13	826.8	36.00	156.99	854.0	6.00	161.24	794.7
36.00	141.55	855.0	38.00	196.56	916.4	9.00	166.75	795.8
Series no 4			Series no 8			14.00	172.37	796.8
0.00	78.35	663.6	1.00	104.20	660.2	24.00	178.37	797.9
2.00	80.03	676.1	3.00	110.83	687.3	40.00	183.04	798.8
4.00	82.17	687.1	5.00	118.23	703.5	Series no 13		
6.00	84.62	698.1	7.00	124.87	717.9	0.20	103.56	769.0
8.00	87.34	710.0	9.00	130.37	731.0	0.60	117.33	773.4
10.00	90.31	724.3	12.00	136.83	749.6	1.00	126.08	778.6
12.00	93.50	742.5	16.00	144.10	776.9	1.50	132.98	782.6
16.00	98.68	774.8	19.00	152.63	807.7	2.50	141.44	786.8
20.04	103.44	787.3	21.00	172.33	850.9	4.00	148.65	789.9
24.00	108.56	796.3	Series no 9			6.00	154.56	792.0
28.00	114.80	806.1	1.00	91.80	664.5	9.00	160.12	793.7
32.00	123.68	819.8	3.00	97.74	681.3	14.00	165.65	795.2
36.00	144.27	851.8	5.00	104.84	696.3	24.00	171.52	796.7
			7.00	111.83	710.4	40.00	175.98	799.8
			9.00	117.92	723.7			
			12.00	125.25	742.5			



Table 2a. Experimental series data. Copper dl-tartrate system

Series no	C_M /mM	C_T^O /mM	C_T^I /mM	C_H^O /mM	C_H^I /mM	E_m^O /mV	E_h^O /mV
1	1.01	1.00		2.00	-3.03	16.45	528.6
2	2.02	2.00		4.01	-6.01	16.50	528.6
3	5.05	5.01		-5.70	10.02	16.40	528.6
4	10.10	10.02		20.04	-29.5	16.40	528.3
5	20.20	20.04		40.1	-59.5	16.40	528.3
6	2.02	10.02		20.04	-19.84	16.35	528.3
7	5.05	10.02		20.04	-19.95	16.35	528.3
8	2.02	25.0		50.1	-49.6	16.40	528.3
9	5.05	25.0		50.1	-49.5	16.40	528.3
10	10.10	25.0		50.1	-49.5	16.40	528.4
11	20.20	50.1		-48.8	100.2	16.40	528.3
12	1.01	0.00	160.3	0.00	21.4	16.35	528.3
13	2.02	0.00	160.3	0.00	20.8	16.35	528.3

Table 2b. Experimental point data. Copper dl-tartrate system.

v	E _m	E _h	v	E _m	E _h	v	E _m	E _h
/ml	/mV	/mV	/ml	/mV	/mV	/ml	/mV	/mV
Series no 1			Series no 10					
2.00	106.94	717.7	16.00	93.74	760.2	2.00	83.37	668.2
6.00	107.85	739.0	20.00	98.78	770.8	5.00	90.26	687.8
10.00	109.25	765.7	24.00	104.24	779.6	7.00	95.58	700.0
14.00	111.73	794.5	28.00	110.94	789.6	9.00	101.02	712.2
18.00	115.09	808.9	32.00	121.12	804.8	12.00	108.67	730.7
22.00	119.25	820.7	36.00	159.53	865.5	16.00	116.85	754.7
26.00	124.33	832.8	Series no 6			20.00	123.53	774.5
30.00	131.45	848.0	0.00	99.77	670.6	24.00	130.69	789.6
34.00	144.66	872.8	3.00	103.32	691.9	28.00	140.56	806.9
36.00	161.12	900.0	5.00	106.64	704.6	31.00	154.68	830.2
Series no 2			7.00	110.34	716.6	33.00	188.21	885.7
2.00	98.68	706.3	9.00	113.99	728.1	Series no 11		
6.00	100.58	728.8	12.00	118.99	745.0	5.00	152.68	817.9
8.00	101.73	741.3	16.00	125.12	768.7	8.00	133.52	785.0
10.00	103.03	755.2	20.00	133.29	794.3	12.00	123.82	761.9
12.00	104.43	770.1	24.00	152.00	830.4	16.00	116.86	742.2
14.00	105.98	781.6	Series no 7			20.00	110.98	727.3
18.00	109.30	794.7	1.00	88.44	674.4	24.00	105.78	716.1
22.00	113.14	805.2	3.00	90.50	686.3	28.00	101.40	707.5
26.00	117.94	816.3	5.00	93.06	697.0	34.00	96.22	697.7
30.00	124.83	830.5	7.00	95.89	707.2	40.00	92.24	690.6
34.00	137.92	854.4	9.00	98.97	717.2	Series no 12		
36.00	154.84	881.9	11.00	102.06	727.7	0.60	125.92	783.5
Series no 3			14.00	106.59	743.9	1.00	133.16	786.0
0.20	130.46	833.6	18.00	112.05	765.0	1.50	139.06	788.0
0.60	123.71	821.7	22.00	117.13	780.1	2.50	146.55	790.2
1.00	119.29	814.1	26.00	122.83	791.9	4.00	153.28	791.8
1.50	115.67	807.5	30.00	130.17	804.9	6.00	158.92	793.0
2.50	110.99	798.6	36.00	156.26	847.9	9.00	164.44	794.0
5.00	104.88	785.9	Series no 8			14.00	170.08	794.9
10.00	99.22	768.8	1.00	103.77	668.1	24.00	176.17	795.9
14.00	96.74	752.5	3.00	109.62	687.2	40.00	180.90	796.8
20.00	94.15	733.1	5.00	116.18	703.3	Series no 13		
31.00	91.44	716.0	7.00	122.29	717.3	0.60	115.42	772.7
40.00	90.42	708.7	9.00	127.46	730.2	1.00	123.69	777.1
Series no 4			12.00	133.72	748.3	1.50	130.52	780.9
2.00	79.93	677.4	16.00	140.88	774.2	2.50	139.03	785.3
6.00	84.19	700.5	19.00	149.40	800.4	4.00	146.36	788.6
10.00	89.41	726.4	21.00	164.14	830.7	6.00	152.41	790.9
13.00	93.62	750.5	Series no 9			9.00	157.97	792.7
16.00	96.92	765.7	1.00	91.36	664.9	14.00	163.57	794.3
20.00	101.11	776.3	3.00	96.63	682.1	24.00	169.53	795.8
24.00	105.57	785.1	5.00	102.94	697.0	40.00	174.04	797.0
28.00	111.38	795.2	7.00	109.23	710.7			
32.00	120.29	810.2	9.00	114.89	723.6			
36.00	147.43	854.3	12.00	121.90	742.0			
Series no 5			16.00	129.44	766.3			
0.00	69.94	650.7	20.00	138.33	791.3			
4.00	74.50	677.6	23.00	150.29	814.6			
8.00	80.42	701.2	25.00	170.62	849.5			
12.00	87.74	733.9						

Table 3. Stability constants of complexes $\text{Cu}_p\text{T}_q\text{H}_r$ formed in acid and neutral copper d-tartrate solutions calculated from data of potentiometric measurements at 25°C and ionic strength 1.00 M with NaClO_4 as neutral salt. Stated errors are equal to three standard deviations. The percentages state the maximum presence of complexes relative to the total amount of copper in the concentration region used for the calculation.

p q r	copper d-tartrate	%	copper dl-tartrate	%	dl-complexes from eq. (16)	
1 1 1	$(3.84 \pm 0.14) \times 10^5$	31	$(3.70 \pm 0.15) \times 10^5$	32		M^{-2}
1 1 0	$(4.3 \pm 0.3) \times 10^2$	23	$(4.5 \pm 0.3) \times 10^2$	30		M^{-1}
1 2 0	$(2.44 \pm 0.14) \times 10^4$	59	$(2.36 \pm 0.11) \times 10^4$	68	$(4.6 \pm 0.5) \times 10^4$	M^{-2}
2 2 0	$(4.00 \pm 0.13) \times 10^8$	67	$(2.04 \pm 0.08) \times 10^8$	58	$(0.2 \pm 0.4) \times 10^8$	M^{-3}
2 2 -1	$(1.60 \pm 0.08) \times 10^4$	29	$(0.98 \pm 0.10) \times 10^4$	23	$(0.7 \pm 0.4) \times 10^4$	M^{-2}
2 2 -2	$(4.4 \pm 0.2) \times 10^{-1}$	66	$(3.0 \pm 0.4) \times 10^{-1}$	32	$(3.1 \pm 1.6) \times 10^{-1}$	M^{-1}
4 3 -4			$(3.4 \pm 0.5) \times 10^{-1}$	15		M^{-2}
4 3 -5			$(1.42 \pm 0.14) \times 10^{-5}$	81		M^{-1}
6 4 -7	$(3.0 \pm 0.3) \times 10^{-6}$	33				M^{-4}
6 5 -7			$(1.1 \pm 0.2) \times 10^{-2}$	56		M^{-3}
8 6 -10	$(4.2 \pm 0.5) \times 10^{-8}$	66				M^{-3}

Figure 1. Emfs versus C_H/C_M , $C_M = C_T = 10$ mM.

represents the copper d-tartrate system,
the dl-system, and full line values
calculated from stability constants of
Table 3.

- a) Emf of the copper amalgam electrode.
- b) Emf of the glass electrode.

Figure 2. Conformation of d-tartrate groups found in the
solid state.

Figure 3. Sketches of tartrate-bridged binuclear complexes
with idealized geometries

- a) tetragonal geometry (dl-complex)
- b) trigonal bipyramidal geometry (dd-complex)
- c) octahedral geometry (dd-complex, broken
lines represent suggested hydrogen bonds)

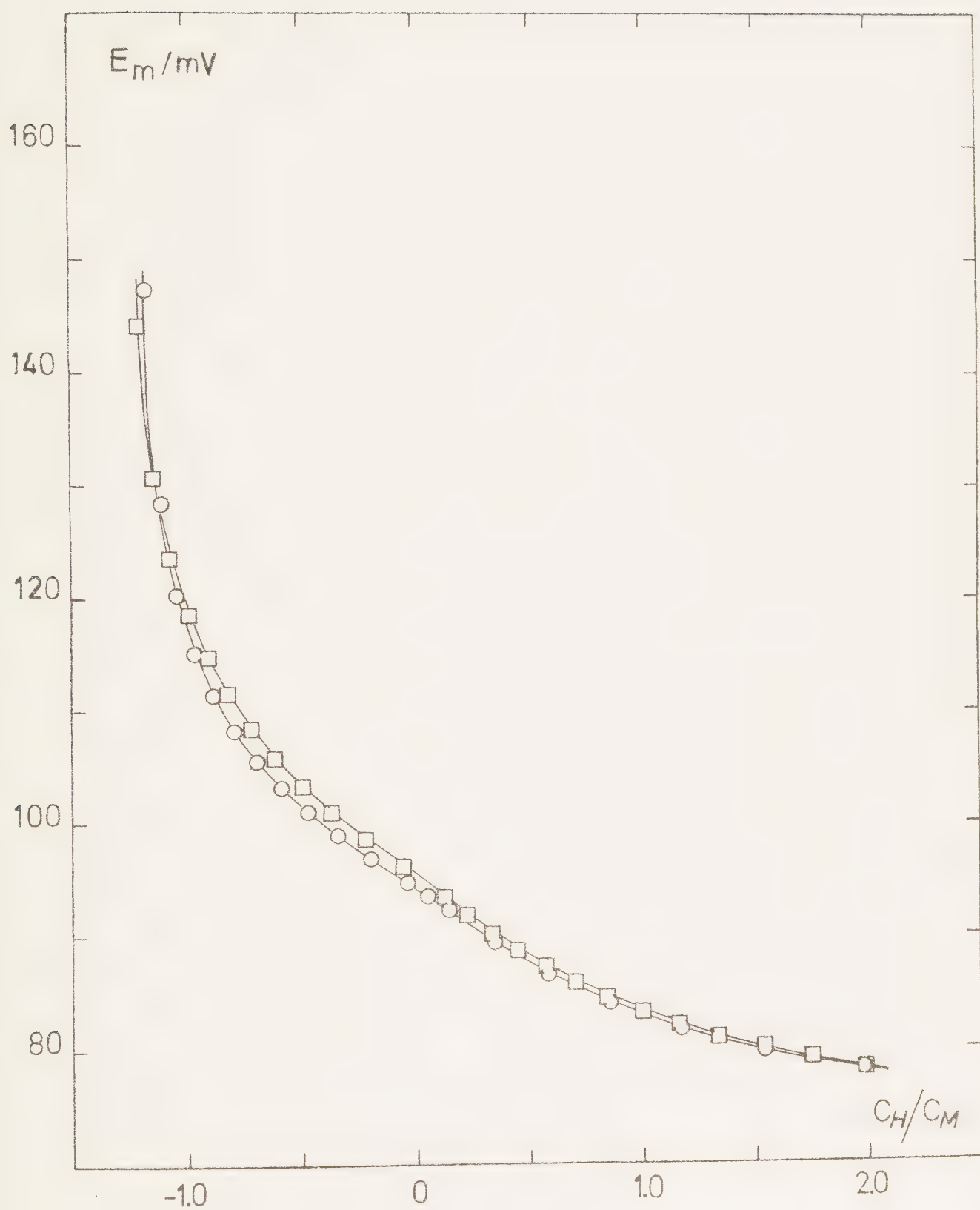


Fig. 1a



Fig. 1b

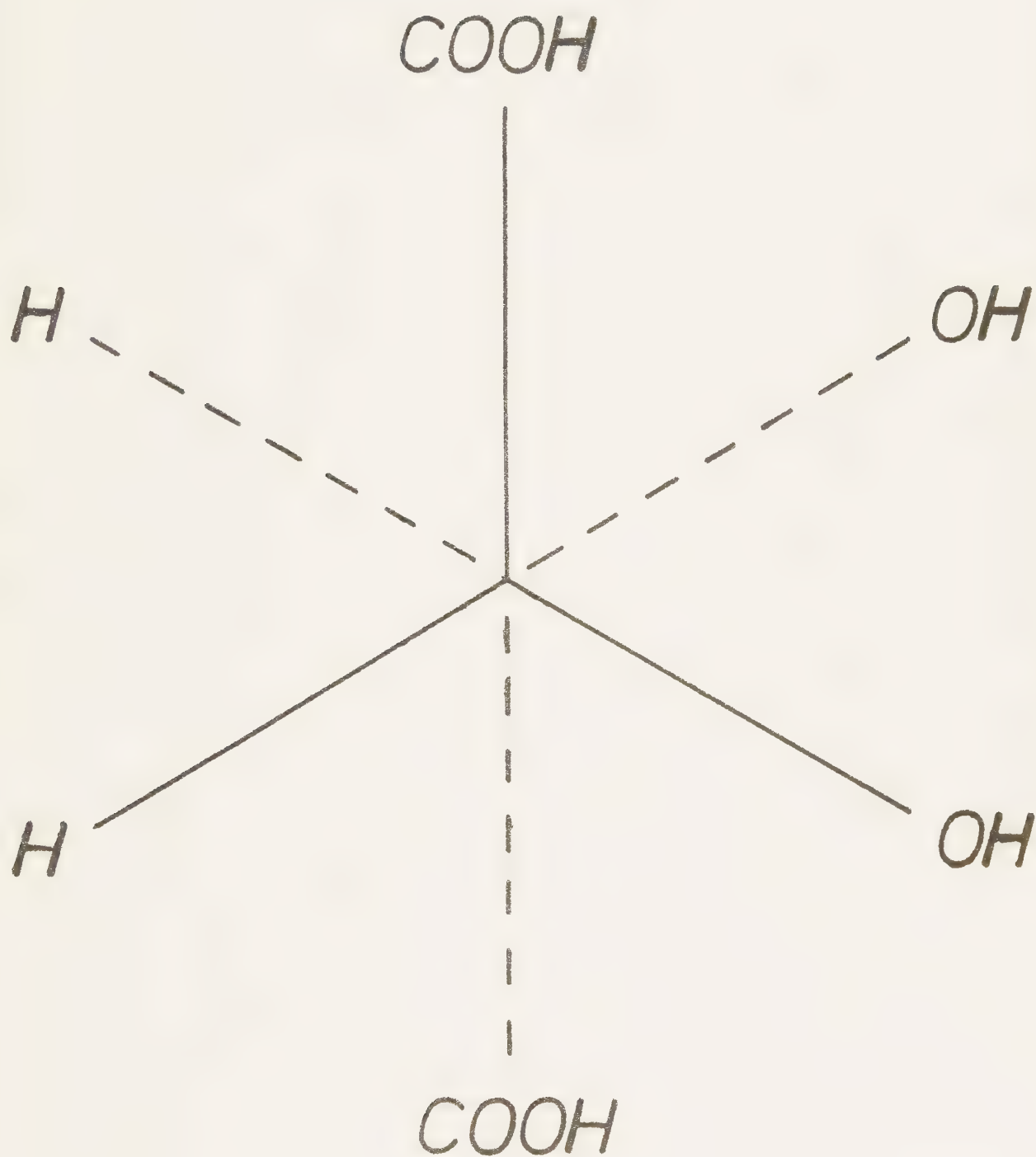


Fig. 2

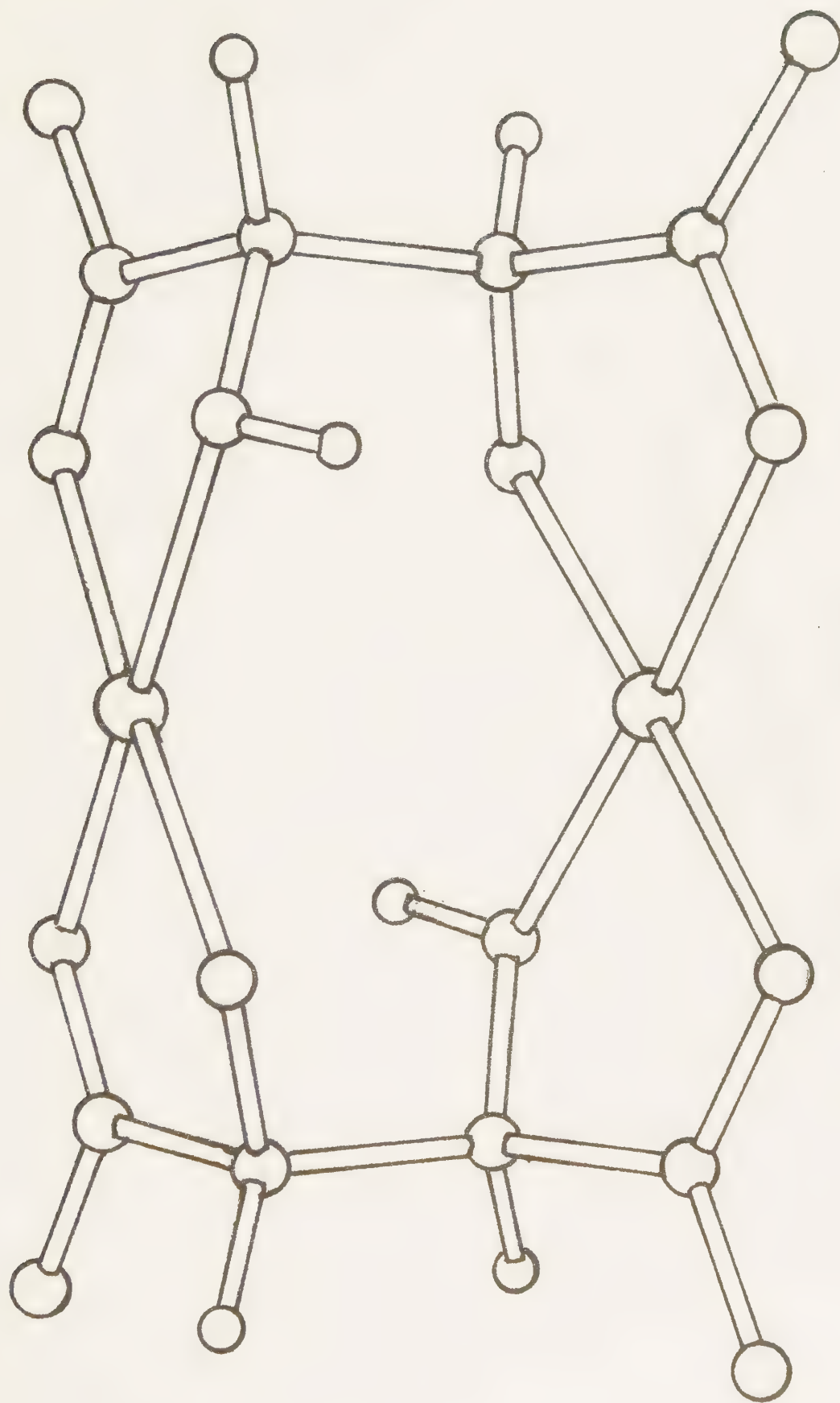


Fig. 3a

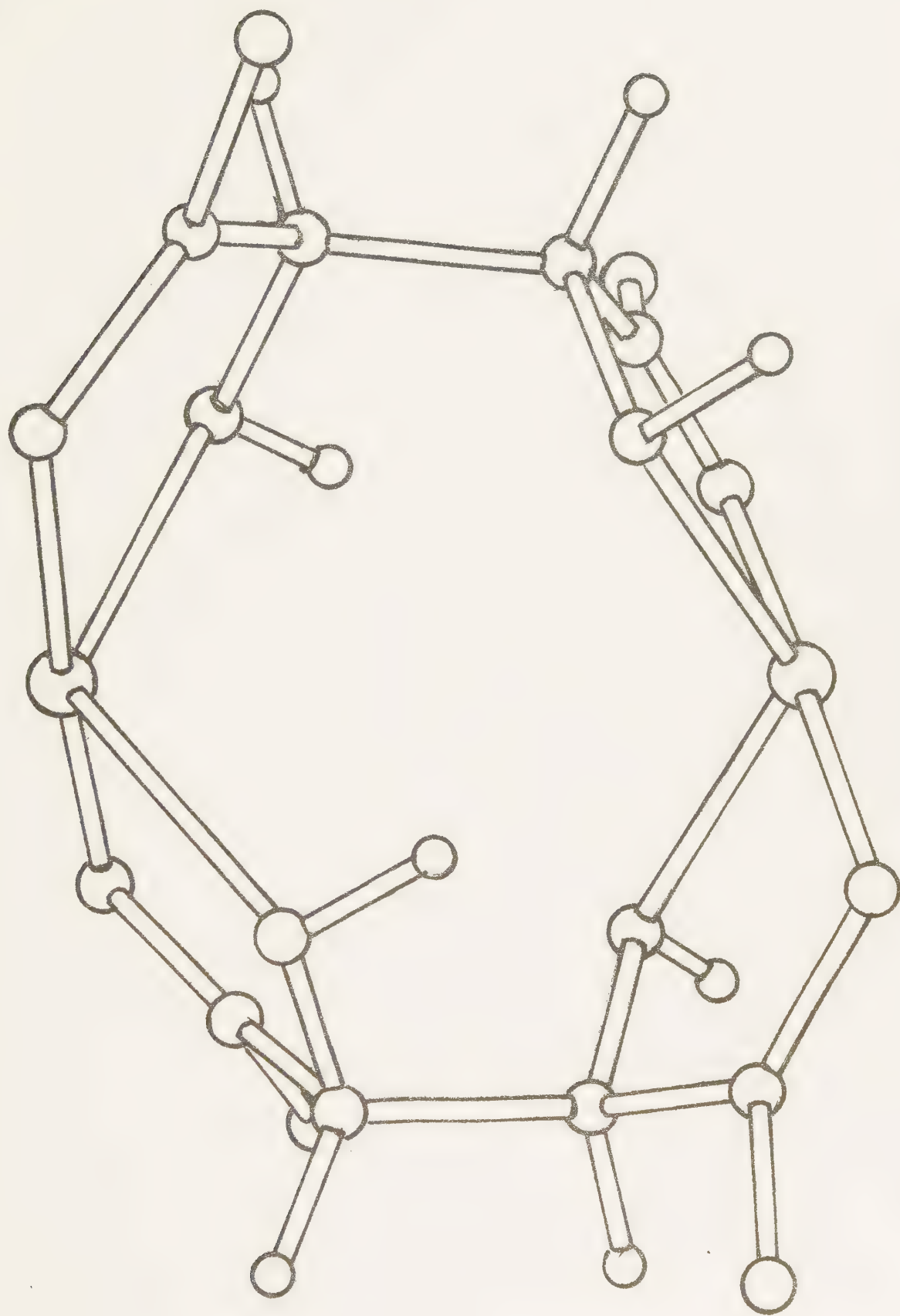


Fig. 3b

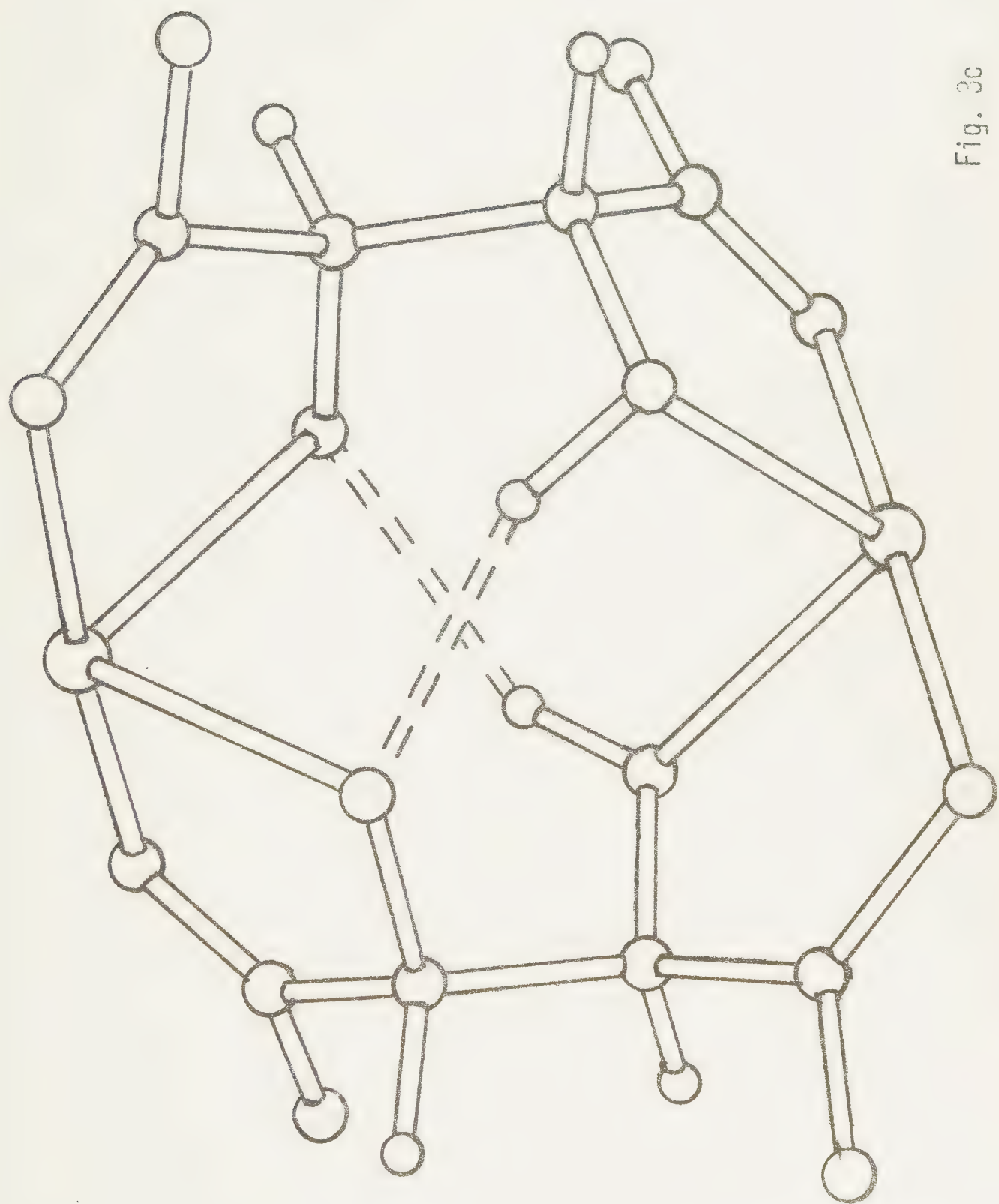


Fig. 3c

On the Structure of a Polynuclear Copper(II) d-Tartrate
Complex in Neutral Aqueous Solution.

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Abstract. The large-angle X-ray scattering and CD-spectra of aqueous solutions of copper(II) d-tartrate with Cu:tartrate:OH = 1:1:1.25 have been recorded. According to potentiometric data the dominating species of the solution should be $\text{Cu}_8(\text{C}_4\text{H}_4\text{O}_6)_6\text{H}_{-10}$. A structure for this complex, based on the dimers $\text{Cu}_2(\text{C}_4\text{H}_4\text{O}_6)_2$ present in the crystal structure of copper d-tartrate trihydrate, $\text{CuC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$, and consistent with both X-ray and CD-data is proposed.

Potentiometric studies of the complex formation between the copper(II) and tartrate ions in aqueous solution show the presence of mono- and binuclear complexes in the acid pH-range. At pH about 4 - in the meso-tartrate system even earlier - a further polymerisation starts ending up with a rapid change of pH to about 8 when about 1.20 to 1.25 mol OH^- /mol Cu^{2+} is added to equimolar solutions of copper and tartrate.¹ The potentiometric data indicate, however, that complexes of different compositions are formed when different kinds of tartrate are used. For the dl- and meso-tartrate systems the complexes $\text{Cu}_4\text{T}_3\text{H}_{-5}$ and $\text{Cu}_5\text{T}_4\text{H}_{-6}$ respectively are predominant in this pH area.* In the d-tartrate system there is, however, a strong indication for the formation of an octanuclear complex, $\text{Cu}_8\text{T}_6\text{H}_{-10}$, but an alternative or simultaneous existence of $\text{Cu}_4\text{T}_3\text{H}_{-5}$ can not be definitely excluded on the basis of the potentiometric data.

Since it may be difficult to distinguish between complexes of high nuclearity from equilibrium measurements alone one would like to get some other support for a suggested complex, or still better some indication of a plausible structure. A fairly compact polynuclear Cu(II)tartrate complex of not too low symmetry must contain groups of identical Cu - Cu distances shorter than 10 Å. Low magnetic moment ($\mu_{\text{eff}} = 1.48$) and vanishing ESR-spectra of neutralized copper tartrate solutions suggest that some of these Cu - Cu distances are even shorter than those of the dimeric units of the solid $\text{CuT} \cdot 3\text{H}_2\text{O}$ (5.26 Å) that displays a normal magnetic moment.²

These facts make it probable that a large-angle X-ray investigation of a concentrated copper tartrate solution may give complementary information. The sharp indication of an equivalence point in the titration curve when 1.25 mol OH^- / mol Cu is added to a copper d-tartrate solution with Cu:T = 1:1 suggests that complexes with an r/p ratio equal to -1.25 are formed quantitatively.³ Preliminary recordings of absorption spectra show that these neutralized

* In the notation $\text{Cu}_p\text{T}_q\text{H}_r$ where $\text{T} = \text{C}_4\text{H}_4\text{O}_6^{2-}$ a negative sign of r means that the complex holds a number of protons lower than that corresponding to the number of $\text{C}_2\text{H}_4\text{O}_6^{2-}$ units in the complex.

solutions obey Beer's law very good, which supports the suggestion that such solutions are practically dominated by one and the same complex. As a solution of this kind - contrary to the corresponding copper dl-tartrate solution - can be made very concentrated we found an attempt with X-rays worthwhile.

EXPERIMENTAL

Preparation of the solutions. Crystals of $\text{CuC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ were dissolved in water by the addition of LiOH . The change in pH during this process was followed by the use of a glass electrode and the addition of LiOH was interrupted at the sharp increase of pH around pH 8 which indicates that the ratio of Cu to OH^- is 1:1.25. The solution was concentrated by slow evaporation and the final concentration of Cu(II) was determined by iodometric titration. Data for the solutions are given in Table 1.

A slow precipitation of Cu(I)oxide on the walls of the vessel was noticed but the amount of Cu(I)oxide formed during the X-ray measurements was found to be quantitatively negligible.

CD-spectra. Circular dichroism spectra were recorded for the solutions subject to the X-ray investigation and for some other copper tartrate solutions of lower total concentration and with $\text{Cu:T} = 1:1$. The pH of the latter solutions was adjusted to 8.0 with sodium hydroxide ($1.25 \text{ mol OH}^-/\text{mol Cu}$), and the ionic medium was kept constant at a formal ionic strength equal to one $\text{mol} \cdot \text{dm}^{-3}$ by the addition of sodium perchlorate. The copper tartrate concentration varied from 2 to 100 mM. CD-spectra were recorded with a JASCO J-41 dichrograph.

X-ray measurements. The X-ray scattering from the free surface of the solution was measured with the use of a diffractometer of the type described by Johansson.⁴ MoK radiation ($\lambda = 0.7107 \text{ \AA}$) was used and measurements were made at every 0.1° from $\theta \approx 1^\circ$ up to $\theta \approx 10^\circ$ where 2θ is the scattering angle. In the region $\theta > 10^\circ$ the intervals were 0.25° . Slit openings of $1/12$, $1/4$ and 1° were used and the data were recalculated to a common slit width from measurements in overlapping regions. 40 000 counts were taken at each angle.

Treatment of the intensity data. All calculations were performed on the UNIVAC 1108 computer at Lund, Sweden, using the program KURVLR.⁵ Corrections for absorption and multiple scattering were considered to be negligible for the present purpose and were not applied. After correction for polarisation the intensities were normalized to a unit of volume containing one Cu atom (Table 1). This was accomplished by comparing the observed intensities, $I_{\text{corr}}(s)$ with the sum of the independent coherent scattering and the incoherent scattering in the range $13 < s < 15 \text{ \AA}^{-1}$ ($s = 4\pi \sin\theta/\lambda$).

Reduced intensities $i(s)$ were calculated according to the expression

$$i(s) = K \cdot I_{\text{corr}}(s) - \sum_i n_i \left[f_i^2(s) + (\Delta f_i'')^2 + \text{del}(s) \cdot I_i^{\text{inc}}(s) \right]$$

where the summation is taken over all atoms in the unit volume. K is the normalization constant; n_i the number of atoms "i" in the chosen unit of volume; $f_i(s)$ is the scattering factor for the atom "i" corrected for the real part of the anomalous dispersion; $\Delta f_i''$ is the imaginary part of the anomalous dispersion correction for atom "i"; $I_i^{\text{inc}}(s)$ is the incoherent scattering from atom "i"; $\text{del}(s)$ is the fraction of incoherent radiation reaching the counter. The scattering factors were taken from Cromer and Waber⁶ for Cu, O, C and Li and from Stewart et al⁷ for H. Values for the incoherent radiation were taken from Cromer and Mann⁸, Cromer⁹ and from Compton and Allison¹⁰. They were corrected for the Breit-irac factor.

Low-frequency additions to the $i(s)$ curve, resulting in peaks in the radial distribution function $D(r)$ below 1 Å, that cannot correspond to interatomic distances, were removed by a Fourier transformation of that part of the $D(r)$ curve, account being taken of contributions of short interatomic distances extending into that region.

The electronic radial distribution function $D(r)$ was calculated from

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{s_{\text{max}}} s \cdot i(s) \cdot M(s) \cdot \sin(rs) \cdot ds$$

The modification function $M(s)$ was chosen to be

$$[f_{\text{Cu}}^2(0)/f_{\text{Cu}}^2(s)] \cdot \exp(-0.01s^2).$$

Intramolecular contributions to the theoretical intensities were calculated from the expression

$$\sum_{\substack{m \neq n \\ m, n}} f_m f_n \frac{\sin(r_{mn}s)}{r_{mn}s} \exp(-b_{mn}s^2)$$

where r_{mn} is the distance between the atoms m and n and b is a temperature factor. Corresponding peakshapes were obtained from these intensities by a Fourier transformation analogous to that used for the experimental intensities.

RESULTS AND DISCUSSION

CD-spectra. There are no systematic deviations from Beer's law in the CD- as well as in the absorption spectra recorded from the copper tartrate solutions with constant ionic medium. This is a strong indication that these solutions contain only one complex in the examined concentration range. The CD-spectra of the concentrated solutions are quite similar to the spectra of the less concentrated solutions (Fig. 1a), which makes it probable that the same complex is present in two kinds of solutions - if not, the complexes should be structurally closely related. The deviations of about 10% in the magnitude of the CD-minima might well arise from the large difference in ionic medium.

The CD-spectra show two minima. Apart from a wavelength shift a similar spectrum with two negative CD-bands is obtained from polycrystalline copper d-tartrate trihydrate in KBr,¹¹ though the short wavelength CD-band is more pronounced in that spectrum (Fig. 16). A negative CD-band in the short wavelength region of the ligand band ($\lambda_{\text{min}} = 690\text{nm}$) is also met in the complex $\text{Cu}_2\text{T}_2\text{H}_{-2}$ in contrast to the two binuclear complexes Cu_2T_2 and $\text{Cu}_2\text{T}_2\text{H}_{-1}$ which are CD-active in the wavelength region about 800 nm.^{11,12}

The building blocks of the structure of $\text{CuT} \cdot 3\text{H}_2\text{O}$ are tartrate-bridged dimers, Cu_2T_2 . The two chelate rings at each Cu(II) are perpendicular to each other.¹³ The formation of the tartrate-bridged dimer also fixes the absolute configuration to be Δ . As the chelate rings are planar within the limits of errors, it has been supposed that

the observed circular dichroism principally originates from the configurational dissymmetry.¹¹ The binuclear complexes mentioned above are supposed to be represented by tartrate-bridged dimers. The angles between the chelate rings may be different in these dimers. The release of two hydroxyl protons would improve the possibilities to the formation of internal hydrogen bonds between opposed tartrate ions which would result in a smaller angle between the chelate rings in $\text{Cu}_2\text{T}_2\text{H}_{-2}$ than in the two other binuclear complexes. This change in coordination geometry is supposed to cause the difference in the CD-spectra of the binuclear complexes. Accordingly the complex $\text{Cu}_2\text{T}_2\text{H}_{-2}$ would be represented by a tartrate-bridged dimer (Fig. 2) very similar to that of $\text{CuT}\cdot 3\text{H}_2\text{O}$, i.e. a dimer with the chelate rings nearly perpendicular to each other.^{1,12}

We suggest that the appearance of the short wavelength minimum in the CD-spectrum of the present complex is an indication of the existence of copper ions with chelate rings in a Δ -configuration and that this state of things arises from associated $\text{Cu}_2\text{T}_2\text{H}_{-2}$ dimers formed as the Cu_2T_2 unit of the crystal structure of $\text{CuT}\cdot 3\text{H}_2\text{O}$. From the potentiometric measurements¹ it is observed that the complex $\text{Cu}_2\text{T}_2\text{H}_{-2}$ is present in the whole pH range where the polymerisation takes place. If the presence of only one complex with $\text{Cu}:\text{T}:\text{H} = 4:3:-5$ is assumed at the equivalence point, the potentiometric data favour the complex $\text{Cu}_8\text{T}_6\text{H}_{-10}$, the formation of which is preceded by a complex $\text{Cu}_6\text{T}_4\text{H}_{-7}$. The appearance of the latter complex may be taken as another indication of Cu_2T_2 -units taking part in the construction of the final complex.

Radial distribution function. The functions $D(r) - 4\pi r^2 \rho_0$ are shown in Fig. 3. As expected from the low atomic number of copper the peaks are not very pronounced but still some features of interest are seen. The peak at 2.0 Å corresponds to Cu-O bond distances. The peak at 3.0 Å is mainly due to water-water interactions but may have contributions from Cu-Cu distances between Cu atoms linked by double hydroxy- or alkoxy-bridges. Such distances are commonly about 3.0 Å or in compounds where Cu-Cu bonds are assumed, much shorter.¹⁴ The peak at 3.5 Å is most probably due to Cu--Cu interactions. In crystal structures Cu atoms linked by one alkoxy-oxygen are normally separated by 3.5 Å.¹⁴ Further it may be noted that at least for the most concentrated solution

there is a small maximum at 5.3 Å. The dimer of $\text{CuT} \cdot 3\text{H}_2\text{O}$ ¹³ has the Cu-Cu distance 5.267 Å.

Molecular models. Encouraged by these findings we prepared molecular models of the dimer Cu_2T_2 , as found in the crystal structure of $\text{CuT} \cdot 3\text{H}_2\text{O}$, and tried to connect three of them by two Cu atoms either via coordinated hydroxide ions or via alkoxy-oxygens of the tartrate ions. The most reasonable structural model is obtained when the dimers are linked by eight Cu-alkoxy-Cu bridges as illustrated in Fig. 4.

The three dimers, A, B and C, are linked by Cu(7) and Cu(8). Cu(7) is bonded to the alkoxy-oxygens O(12) and O(14) of dimer A and O(11) and O(13) of dimer B. With the Cu(1)--Cu(2) vectors of the adjacent dimers perpendicular to each other these four alkoxy-oxygens form an almost perfect square planar surrounding of Cu(7). With all Cu(7)-O bond distances 2.0 Å the distances Cu(7)-Cu(1)_A and Cu(7)-Cu(2)_A are 3.6 Å while the distances Cu(7)-Cu(1)_B and Cu(7)-Cu(2)_B are 3.4 Å. This difference in length is due to the fact that O(11) and O(13) form 2.4 Å bonds to Cu within the dimer while the corresponding bonds of O(12) and O(14) are 2.0 Å. Cu(8) is situated correspondingly between dimer B and dimer C.

The dimer as found in the crystal structure has no symmetry element but there is an approximate 2-fold axis perpendicular to the Cu(1)--Cu(2) vector. In our model Cu(7) and Cu(8) are situated on this 2-fold axis; adjacent dimers are translated along the axis and rotated around it. When this rotation is made about 100° the outer carboxy-oxygens situated in the region between the dimers (e.g. O(21)_A, O(23)_A, O(22)_B and O(24)_B between dimer A and B) come in positions suitable for hydrogen bonding to coordinated water molecules. The O(water)--O(carboxylate) separations are around 2.8 Å and each water molecule is fairly close to the plane of the corresponding hydrogen bond accepting carboxylate group. Eight hydrogen bonds, each between a water molecule of one dimer and outer carboxy-oxygen of the adjacent dimer, may be formed in this way as indicated in Fig. 4.

The model is capable of explaining the release of ten protons; eight protons must be given off in forming the bonds to Cu(7) and Cu(8). If

in addition one hydroxyl group in each of the outer dimers releases one proton, the complex may be terminated by two short intramolecular hydrogen bonds.

Difference functions. The model just described has eight Cu--Cu distances close to 3.5 Å, one at 4.7 Å, three at 5.3 Å and eight Cu--Cu distances around 6 Å. In addition there are four pairs of Cu--Cu distances in the region 7 - 10 Å. The low frequency of these longer distances makes them less probable to be detected in the RDF. Peaks or at least maxima in the RDF are present at 3.5 Å, 5.3 Å and 6 Å but because of the low atomic number of copper, Cu-ligand atom interactions may disturb the picture, and the coordinates of all atoms within the complex would be needed to get a reliable calculated peakshape. Approximate atomic positions were calculated using the coordinates of the atoms within the dimer as found in the crystal structure of $\text{CuT} \cdot 3\text{H}_2\text{O}$.¹³ A position of Cu(7) was found by placing it 2.00 Å from each of the alkoxy-oxygens $\text{O}(11)_B$ and $\text{O}(13)_B$ and equidistant between $\text{Cu}(1)_B$ and $\text{Cu}(2)_B$. The position of Cu(8) was found in a corresponding way. The dimer was then translated along and rotated about Cu(7)--Cu(8) as described above. With the coordinates thus obtained the short Cu--Cu distances are 3.40 Å and 3.60 Å and the Cu(7)--Cu(8) distance 4.63 Å. Four of the Cu-Cu distances around 6 Å are 5.72 Å and four 6.12 Å.

The different surroundings of the dimers in the suggested complex as compared to the crystal structure probably lead to slight changes in the atomic positions and the peakshape obtained by using the constructed set of atomic coordinates can only be regarded as an approximate picture of the complex. This is especially true for the interactions between atoms of dimer A and atoms of dimer C which affect the peakshape in the region $r > 8.5$ Å. At these long distances the errors may well accumulate to several multiples of 0.1 Å, and in addition the temperature factors may be larger. For these reasons the calculated peakshape given in Fig. 3 is dotted for large distances. The b-values used in calculating the peakshape are given in Table 2. They are probably too low for the longer distances but it has not been regarded as worthwhile to make any further guesses about them.

The difference $D(r) - 4\pi r^2 \rho_0 - \Sigma P_{pq}$ is shown in Figs. 3b and c. ΣP_{pq} includes all interactions within the complex as well as the contributions from Li-O bond distances and from distances within the uncomplexed ligands. The water peak at 2.9 Å increases as the number of water molecules of the stoichiometric volume increases. It has the same form for both solutions and there is no indication that the proposed number of Cu-Cu interactions at 3.5 Å should be too large. Distances within the dimers do not contribute very much to ΣP_{pq} around 3.5 Å, so provided the complex is built up from dimers, the peak at 3.5 Å in the experimental function has to be associated with the linking of the dimers. The distinct shape of the peak makes it probable that one kind of distance gives a dominating contribution to the peak and this distance should certainly be Cu-Cu. As a matter of fact we have found no other way of linking the dimers in order to make a structure for $Cu_8T_6H_{-10}$ nor found any other reasonable structure for $Cu_8T_6H_{-10}$ or $Cu_4T_3H_{-5}$, that gives such a high number of short Cu-Cu distances that the one proposed.

The peak at 4.0 Å most probably results from interactions of the type Cu(i)--W(i) where W(i) is a water molecule of the second coordination sphere around Cu(i). With the hydrogen bond distance O--W = 2.8 Å and the bond angle Cu-O-W 109.5° the distance Cu--W is 3.9 Å for Cu-O = 2.0 Å and 4.2 Å for Cu-O = 2.4 Å. The shoulder just below 5 Å is characteristic of the structure of pure water as is a flat minimum between 5 and 6 Å.¹⁷ Minima as broad and deep as those in Figs. 3b and c are found also in other investigations of solutions of complexes large enough to account for most of the interatomic interactions in this region e.g. heteropoly-molybdates¹⁵ and lanthanid oxydiacetates.¹⁶

A discussion of the difference curve at larger distances does not seem fruitful because of the approximity of the calculated peakshape for the complex in this region and also because intercomplex and complex-bulkwater interactions - even if highly damped - can no longer be ignored. It is however interesting to note that the addition of second sphere of water molecules in the molecular model using normal hydrogen bond distances and angles, results in a large number of Cu(i)--W(j) distances around 7 Å and around 8 Å

(W(j) belongs to the second sphere around Cu(j), $j \neq i$).

Obviously our assumption that a complex $\text{Cu}_8\text{T}_6\text{H}_{-10}$ of the proposed structure is the dominating species of the investigated solution is consistent with the X-ray scattering data. But since the radial distribution curve only gives a one dimensional representation of the three dimensional complex in the solution the possibility can not be excluded that other structural models giving a good explanation of the experimental data may be derived. Nevertheless the fact that a plausible model of a complex $\text{Cu}_8\text{T}_6\text{H}_{-10}$ can be constructed which is based on dimers with a geometry present in the solid state and according to CD-spectra probably also represented in solution, and which in a satisfactory way explains the X-ray diffraction data, must be considered to support the potentiometric findings of a complex of this composition in solution.

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Table 1. Composition of the solutions.

$C_{\text{Cu}} = 1.75 \text{ M}$		$C_{\text{Cu}} = 1.00 \text{ M}$	
Concentration in $\text{mol} \cdot \text{dm}^{-3}$	Number of atoms in the stoichio- metric volume, V	Concentration in $\text{mol} \cdot \text{dm}^{-3}$	Number of atoms in the stoichio- metric volume, V
Cu	1.75	1.00	1.00
O	59.4	57.3	57.3
C	7.0	4.00	4.00
L	2.19	1.25	1.25
H	103	105	105
$V/\text{\AA}^3$	948	1660	
$\rho_{\text{O}}/\text{el}^2 \cdot \text{\AA}^{-3}$	156.0	232	

Table 2. Temperature factors, b , used in the calculations of the peakshape function.

Atoms	Distance range ($\text{\AA}$)	$b/\text{\AA}$
Cu--Cu	$r < 4$	0.001
	$4 < r < 5.5$	0.005
	$r > 5.5$	0.01
Cu--O, Cu--C	$r < 4.5$	0.005
	$r > 4.5$	0.01
light--light	whole range	0.005

- Fig. 1 a) Absorption and circular dichroism spectra of aqueous copper d-tartrate solutions at pH = 8.0 and constant ionic medium ($I = 1\text{ M}$), fulldrawn, and the circular dichroism spectrum of the 1.75 M copper d-tartrate solution used for the X-ray study, dashed line.
- b) Circular dichroism spectrum of solid copper d-tartrate trihydrate dispersed in KBr.¹¹
- Fig. 2 Tartrate-bridged dimeric structure with the chelate rings at right angles to each other as suggested for the complex $\text{Cu}_2\text{T}_2\text{H}_{-2}$. The dashed lines represent hydrogen bonds.
- Fig. 3 a) Upper fulldrawn curve. Calculated peakshape for the sum of Cu-light atom and light atom - light atom interactions within the suggested complex $\text{Cu}_8\text{T}_6\text{H}_{-10}$. Contributions from Li-O bond distances and distances within uncoordinated ligands are included.
- The dashed curve represents the complete sum, ΣP_{pq} , i.e. Cu-Cu interactions within the complex - lower fulldrawn curve - have been added.
- b-c) Upper fulldrawn curves show the experimental function $D(r) - 4\pi r^2 \rho_0$. The lower fulldrawn curves represent the difference function $D(r) - 4\pi r^2 \rho_0 - \Sigma P_{pq}$. ΣP_{pq} (from 3 a) is inserted in 3 b, the dashed line. b) $C_{\text{Cu}} = 1.75\text{ M}$; c) $C_{\text{Cu}} = 1.00\text{ M}$. All curves in Fig. 3 are calculated for a stoichiometric volume containing one copper atom.
- Fig. 4 The suggested structure of $\text{Cu}_8\text{T}_6\text{H}_{-10}$. Single dashed lines represent hydrogen bonds.

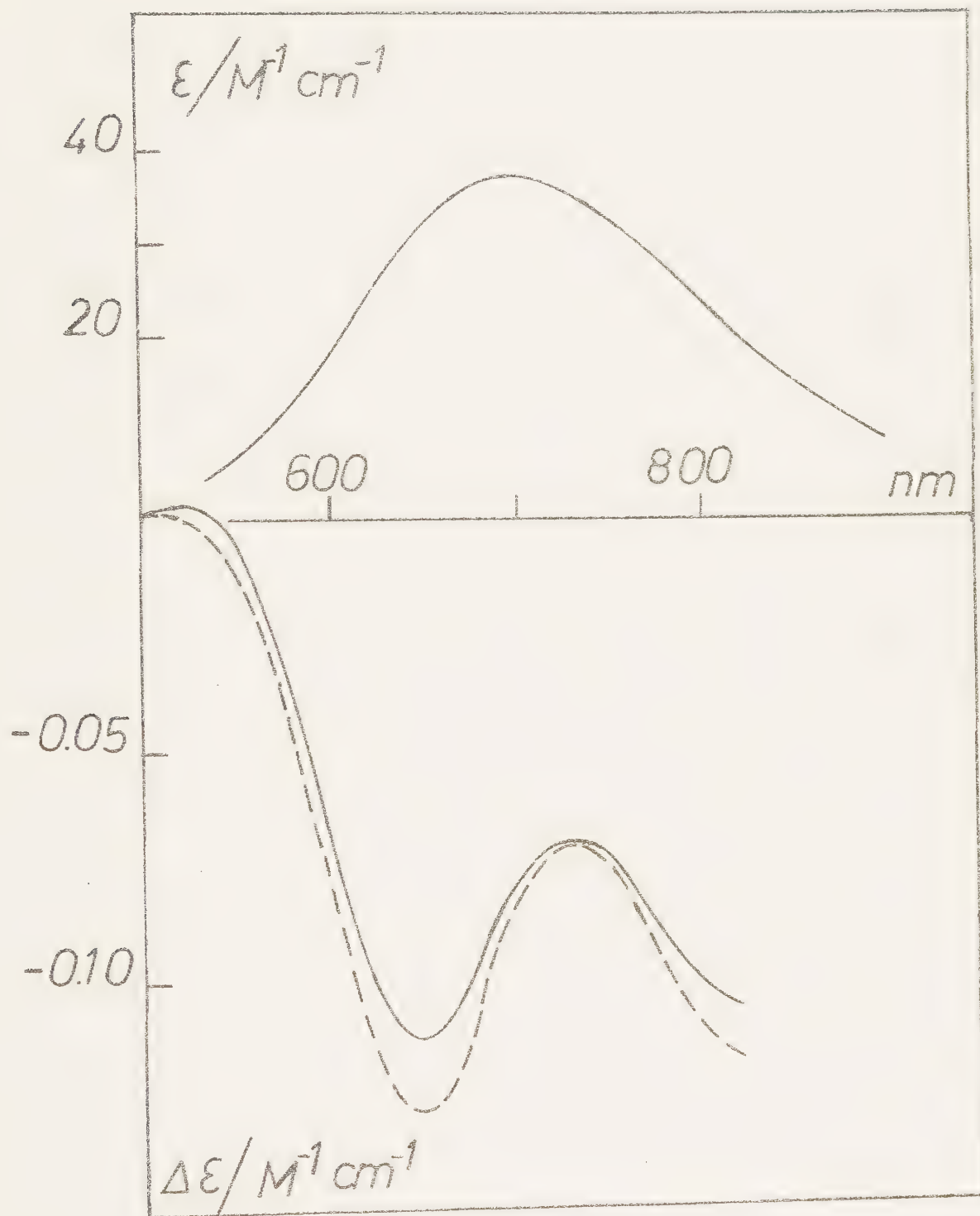


Fig. 1a

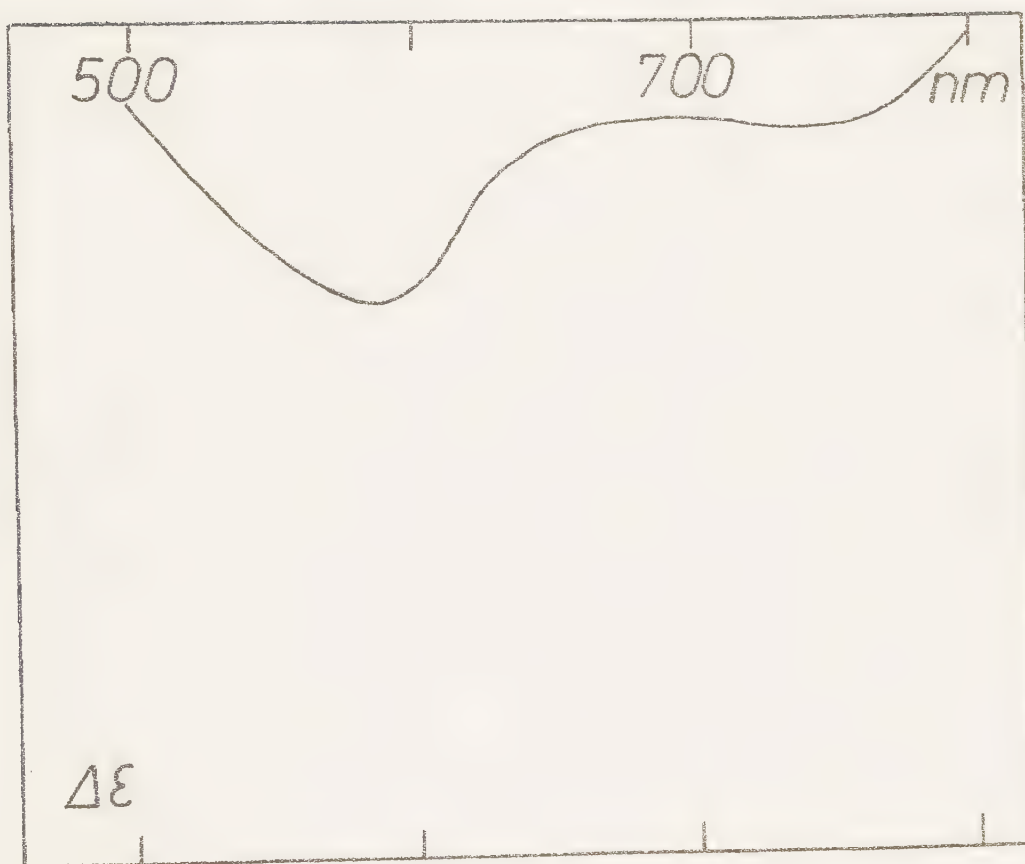
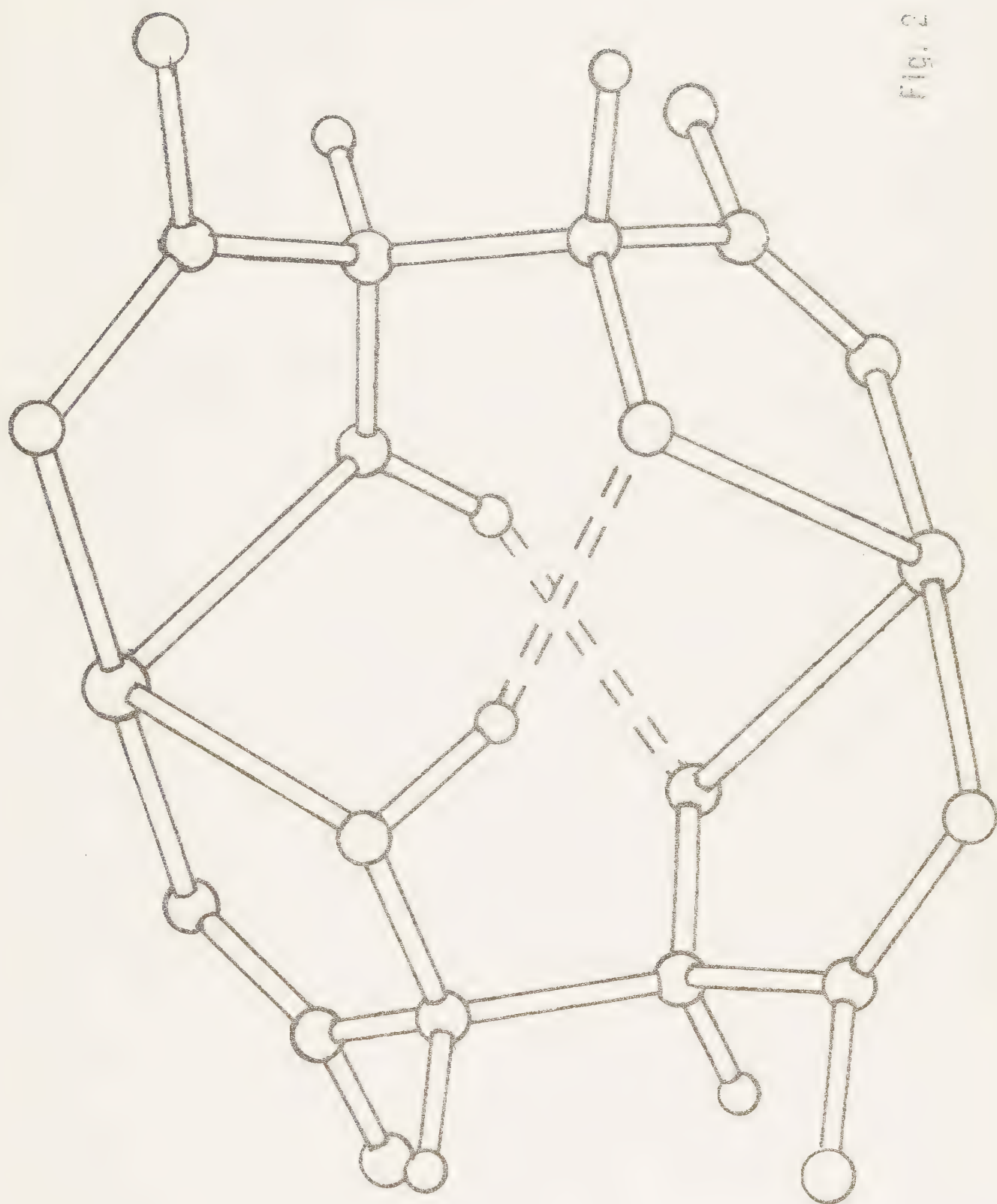


Fig. 1b

Fig. 2



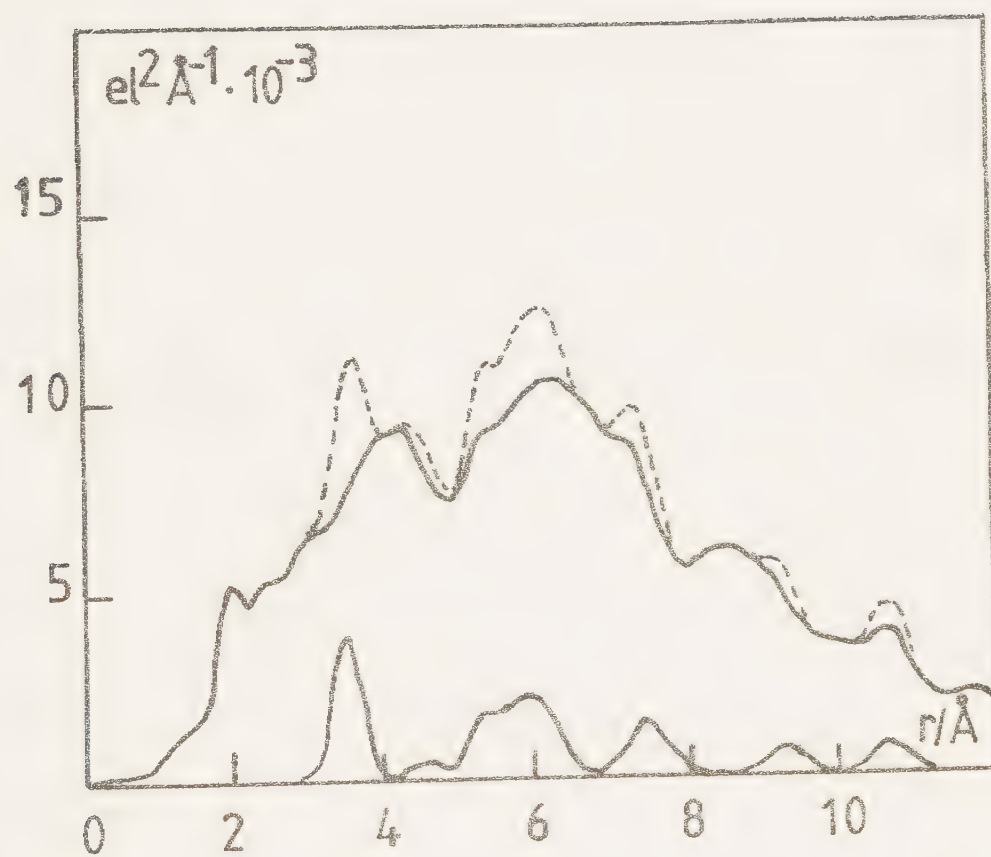


Fig. 3a

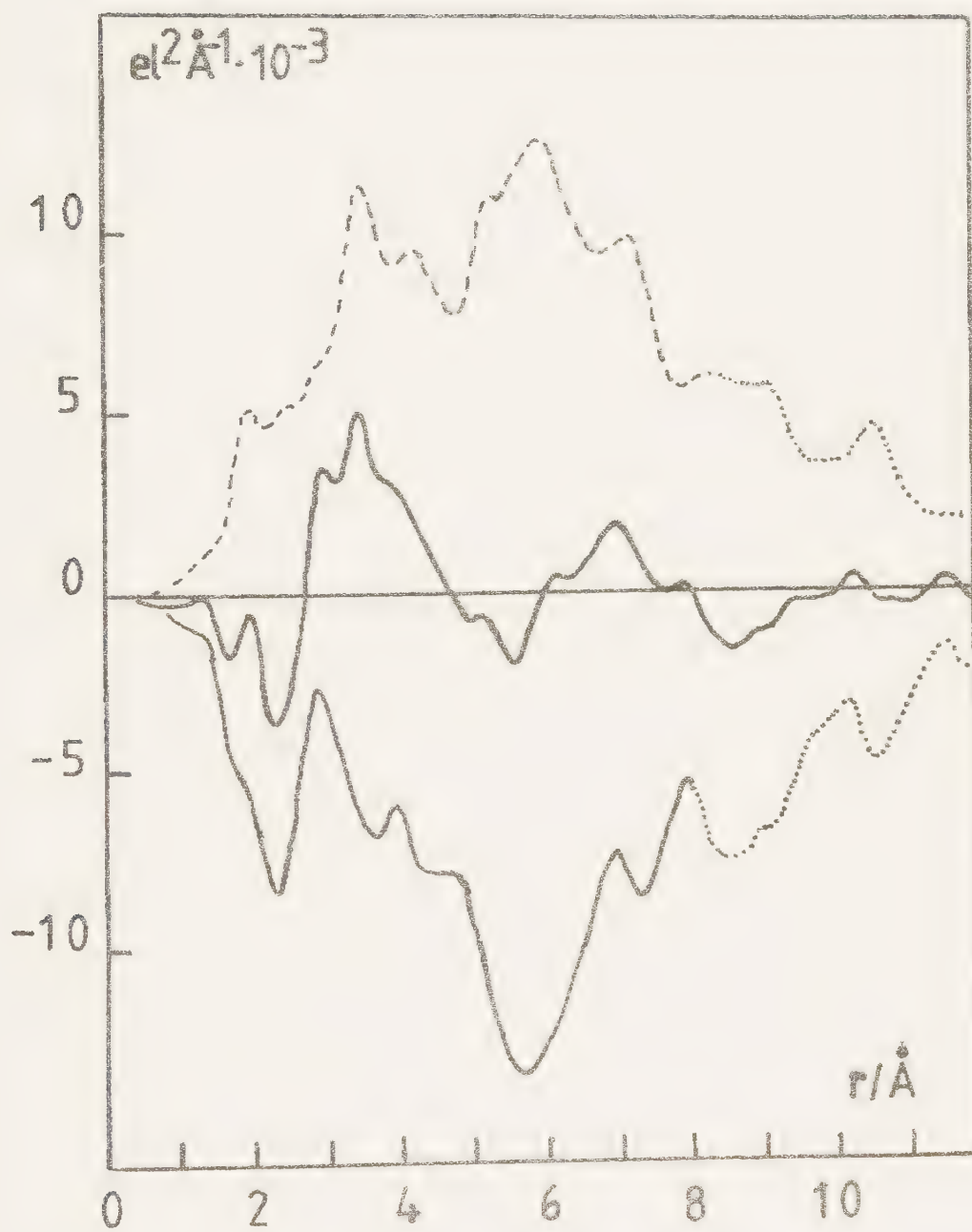


Fig. 3b

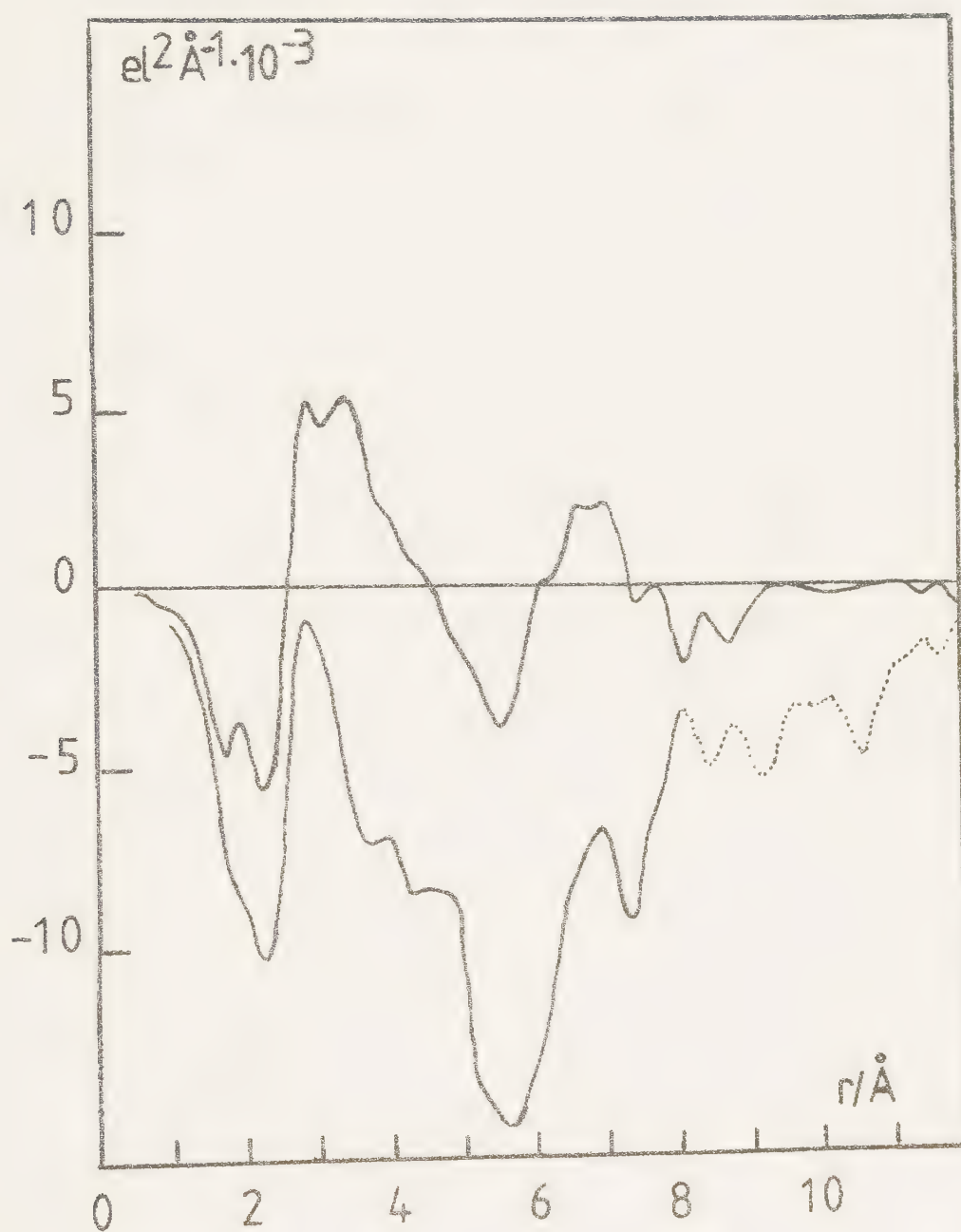


Fig. 3c

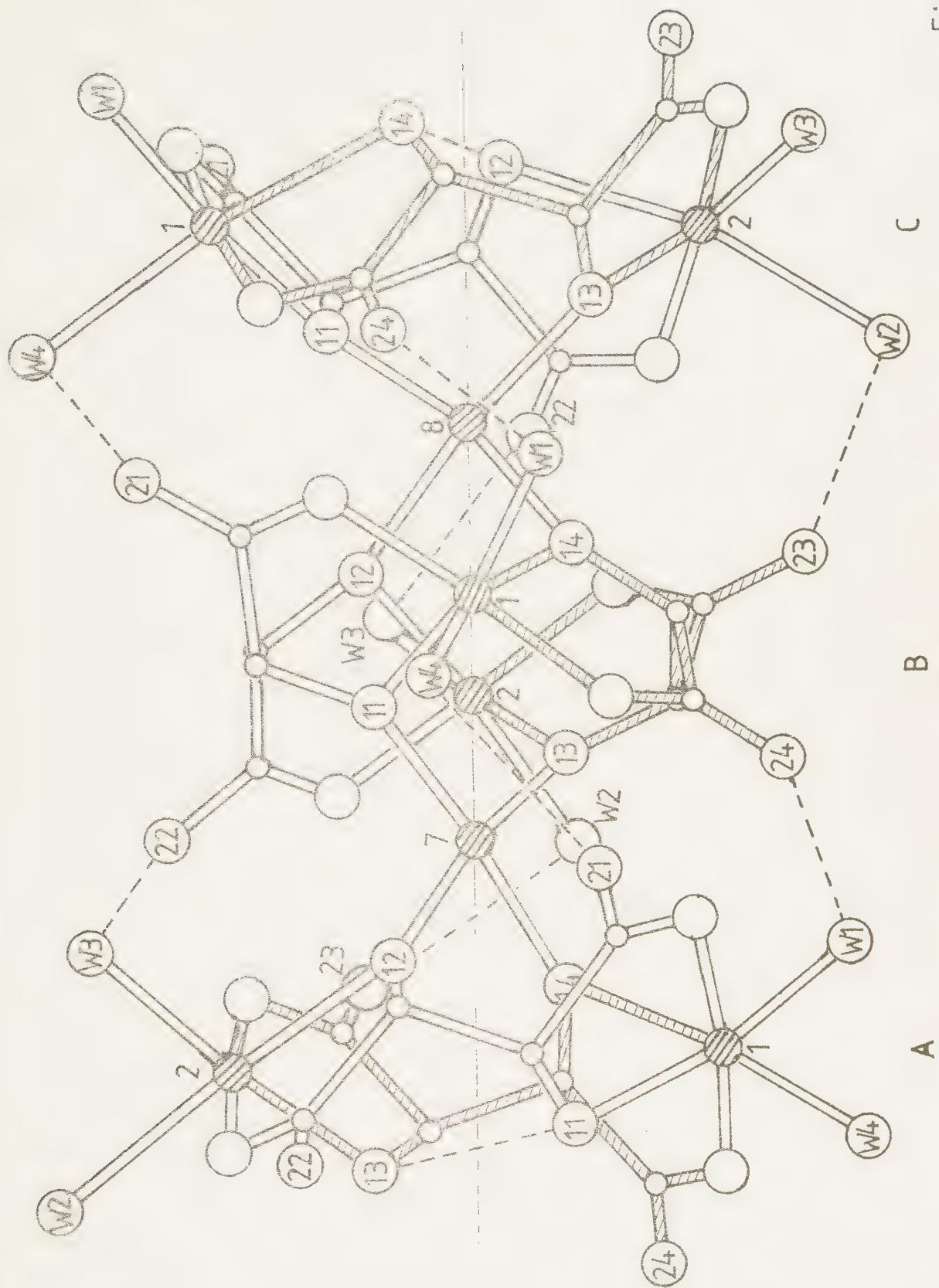


Fig. 4

Complex Formation in the Copper(II) meso-Tartrate System
in Acid and Neutral Aqueous Solution.

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Abstract

The complex formation in aqueous solution between the copper(II) ion and meso-tartaric acid has been studied in the acid and the neutral pH-range at 25°C. A potentiometric method with the use of glass and copper amalgam electrodes has been applied. A formal ionic strength equal to one mol·dm⁻³ was maintained by the addition of sodium perchlorate.

Experimental data were analysed as to the complexes formed and their stability constants. At pH < 4 the system is characterized by an equilibrium between mono- and binuclear species, CuT, CuTH and CuT₂, and Cu₂T₂ respectively (T = C₄H₄O₆²⁻), though the binuclear complex does not play such an important role as the binuclear complexes in the copper d- and dl-tartrate systems.

At pH > 4 polynuclear complexes are formed. In neutral solutions a complex Cu₅T₄H₋₆ is formed almost quantitatively.

Introduction

Whereas the complex formation between d- and dl-tartrate and various metal ions has been subject to much attention the studies on the complex formation of the meso-tartrate ion are relatively few. For the copper(II) meso-tartrate system there are only two investigations reported on a quantitative determination of complexes formed in aqueous solution. Both of them concern the acid pH-range. Ramamoorthy and Manning [1] find a first and a second mononuclear complex while Ostacoli et al. [2], besides

mononuclear complexes, introduce a binuclear complex, $\text{Cu}_2\text{T}_2\text{H}_{-2}$ ($\text{T} = \text{C}_4\text{H}_4\text{O}_6^{2-}$). The stability constants of the mononuclear complexes are larger than the corresponding ones in the copper d-tartrate system. It is also noted from a comparison of protolysis constants that the meso-tartrate ion shows a greater basicity than the d-tartrate ion [1,2].

Much of the work on the copper meso-tartrate system concerns the characterization of solids precipitated from solutions at different values of pH [3-6]. The similarity as to the composition of these solids compared to d- and dl-tartrates prepared under similar conditions is emphasized [3,4]. For the pH-region used in this work it is observed that the trihydrates $\text{CuT} \cdot 3\text{H}_2\text{O}$ can be precipitated from acid copper tartrate solutions, using either d-, dl- or meso-tartrate [7,8] and that solid phases containing a stoichiometric unit $\text{Cu}_4\text{T}_3\text{H}_{-5}$ can be prepared from neutralized copper d-, dl- and meso-tartrate solutions [9,10,5]. The solids of the latter kind as well as their solutions show the same reduction of the magnetic moment ($\mu_{\text{eff}} = 1.48 \mu_{\text{B}}$) and similar ESR-spectra [11] indicating polymeric units with copper ions linked by exchange interactions.

Besides the difference in configuration it has been shown from diffraction investigations on the crystal structures of meso-tartaric acid [12] and various meso-tartrates [8,13,14] that the meso-tartrate molecule takes a staggered conformation with the carboxyl groups in an adjacent position (Fig. 1) whereas the d-tartrate molecule places them in a transoid position. Considering

those differences in configuration and conformation it seems hardly probable that the meso-tartrate ion would show a behaviour equivalent to the d- and dl-tartrates in the formation of polynuclear complexes. As shown by Tapscott [15] the formation of tartrate-bridged binuclear complexes, which are prevalent in many d- and dl-tartrate compounds [16] , should be less favourable for meso-tartrate. In accordance with this, ESR-measurements on acid copper meso-tartrate solutions indicate that these solutions should be dominated by species having very weak magnetic interactions between metal centers [17]. The crystal structures of the trihydrates display similar conditions in that the meso-tartrate structure is built up from copper tartrate chains whereas in the d-tartrate structure a typical tartrate-bridged dimer can be discerned [8].

In a previous work [18] a comparative study of the copper d- and dl-tartrate systems in acid and neutral aqueous solution was performed by the use of a potentiometric method. In the present work that study is extended to the copper meso-tartrate system in order to produce a basis for a comparison of the meso-tartrate system to the other two systems under equivalent conditions. Consequently the experimental arrangements are the same as in the previous work i.e. the concentrations of the free ions Cu^{2+} and H^{+} are determined simultaneously by the use of a copper amalgam and a glass electrode and a common reference electrode. The measurements were performed at 25°C as titrations in a sodium perchlorate medium and with an ionic strength equal to one $\text{mol}\cdot\text{dm}^{-3}$.

Methods

The mathematical treatment of measured data is the same as that of Ref. 18. Therefore those matters will be recapitulated briefly and for details the reader is referred to the previous paper.

The stability constants of the complexes used for the description of data are calculated by minimizing the sum

$$S = \sum_i [w_{m,i} (E_{m,i}^{\text{exp}} - E_{m,i}^{\text{cal}})^2 + w_{h,i} (E_{h,i}^{\text{exp}} - E_{h,i}^{\text{cal}})^2 - w_{mh,i} (E_{m,i}^{\text{exp}} - E_{m,i}^{\text{cal}}) (E_{h,i}^{\text{exp}} - E_{h,i}^{\text{cal}})]. \quad (1)$$

The emfs E_m and E_h are related to the free concentrations of Cu^{2+} and H^+ according to

$$E_m = E_m^0 - S_m \ln m + E_j \quad (2)$$

$$E_h = E_h^0 - S_h \ln h + E_j \quad (3)$$

where E_j is a correction term.

As the emfs are measured simultaneously there will be a considerable correlation between them in some concentration regions which is the reason for the addition of the third term in Eq. 1. The weights of Eq. 1 have been calculated analytically from the expressions accounting for the relations between the emfs and the variables which are considered as sources of error. As in Ref. 18 the variables most serious in regard to correlation, viz. the sodium hydroxide concentrations of the titrator solutions, have been treated as unknown parameters. The values

of E^0 in Eqs. 2 and 3 have been determined separately. The correction term, E_j , has been approximated to a sum of linear terms, each term representing an electrolyte of the complex solution. The terms representing the complex electrolytes are supposed to be negligible as the total copper concentration is low.

The parameters to be varied in order to find a minimum of the function S in Eq. 1 are thus the stability constants β_{pqr} and one concentration variable for each titration series. The values of β_{011} and β_{012} i.e. the protolysis constants of the meso-tartaric acid are determined separately. For the minimization process the FORTRAN subroutine STEPIT [19] has been used.

Experimental. Copper perchlorate, sodium perchlorate and copper amalgam are the same as used in Ref. 18.

The meso-tartaric acid, meso- $C_4H_4O_6 \cdot H_2O$ (Fluka purum) was recrystallized three times (m.p. 146-148°C).

The preparation of the solutions and the measuring procedure were identical with those of Ref. 18. Stable emfs were obtained after a few minutes.

Measurements and results

The concentration region covered is the same as in the previous work. The measurements are confined to the acid and neutral pH range. Copper and tartrate concentration ranges may be read from Table 1a and measured data from Table 1b. Fig. 2 shows represen-

tive titration curves with corresponding curves for the copper d-tartrate system inserted for comparison.

The protolysis constants of meso-tartaric acid were calculated numerically from data measured under the same experimental conditions as the other measurements. The following constants were obtained,

$$K_{a1} = (1.314 \pm 0.006) \cdot 10^{-3} \text{ M}$$

$$K_{a2} = (7.52 \pm 0.02) \cdot 10^{-5} \text{ M.}$$

The constants are given with 99% confidence intervals.

Emf corrections. Emf correction coefficients from Ref. 18 were used except for the coefficients of the meso-tartrate species which were determined in the same way as in Ref. 18. The following coefficients were obtained.

Na_2T	NaHT	H_2T	
16	-10	-17	$\text{mV} \cdot \text{M}^{-1}$.

As in the previous measurements deviations of the sodium perchlorate concentration from one $\text{mol} \cdot \text{dm}^{-3}$ and in some cases high tartrate(2-) concentrations give the largest contributions to E_j .

The existence of several complexes have been tested. As in the case of copper d- and dl-tartrate systems it appears that polynuclear as well as hydrolysed complexes are formed and the same difficulties to find an exclusive set of complexes for the de-

scription of the data is experienced. For this reason the existence of complexes with a low concentration - less than 10-15% relative the total copper concentration - is considered as very uncertain and such complexes are consequently omitted.

In the series with the highest copper concentration, 20 mM, the onset of a precipitation of copper tartrate - as in the d-tartrate system - disturbed the measurements. A small discrepancy in the fitting of the data in the most critical pH-range of these series is attributed to the precipitation. The stability constants presented in Table 2 are obtained from calculations at which the 20 mM series have been omitted. It should also be noted that there is a considerable correlation between the calculated values of some constants, especially between β_{110} and β_{220} ($\rho_{110,220} = -0.83$).

As for the copper d- and dl-tartrate systems the meso-system is described in acid solutions in terms of mono- and binuclear complexes viz. CuTH , CuT and Cu_2T_2 . The mononuclear complexes are, however, more stable than corresponding d-tartrate complexes and - contrary to the situation in the d- and dl-tartrate systems - they are more abundant than the binuclear complexes.

The continued polymerisation accompanying the increase of pH starts somewhat earlier in the meso-tartrate system. At pH 4 complexes containing more than two copper ions are already predominant. Ostacoli et al. [2] report a hydrolysed binuclear complex, $\text{Cu}_2\text{T}_2\text{H}_{-2}$, but the existence of hydrolysed binuclear

complexes cannot be verified from the data of this study. The formation of such complexes is probably depressed by the early appearance of the more condensed species. As in the d- and dl-systems there is a rapid change of pH - however not so large as that of the d-tartrate system - when equimolar copper meso-tartrate solutions are neutralized, but it appears earlier and is practically completed when $C_H/C_M = -1.20$. The calculations show that the change of pH corresponds to an almost quantitative formation of the complex $Cu_5T_4H_{-6}$. From copper meso-tartrate solutions of a corresponding pH, solids containing the stoichiometric unit $Cu_{10}T_7H_{-12}$ have been prepared [6]. However, the addition of a complex with that composition to the set of complexes does not improve the fitting of the data. The formation of complexes with the ratio Cu:T:H equal to 4:3:-5, which are important in the d- and dl-systems and to which corresponding solids have been prepared in the meso-tartrate system [5], cannot be established with acceptable statistical significance from the present data, nor excluded.

As was the case in the d- and dl-systems appreciable amounts of some other species appear in the range $-1.20 < C_H/C_M < 0$. They have been characterized as $Cu_5T_4H_{-5}$ and $Cu_6T_4H_{-7}$ but the difficulty of a unique choice of complexes for description of the data in this pH-range has to be admitted.

Discussion

A comparison with the single study of the copper meso-tartrate

system performed under similar experimental conditions as this study, viz. that of Ostacoli et al. [2], shows a consistency in the predominance of the mononuclear complexes in acid solutions and a fairly good agreement between the stability constants of CuTH and CuT. However the description of the data of this work requires the introduction of the binuclear complex Cu₂T₂ even if this complex takes a less important part of the complex formation than the corresponding complex in the d- and dl-systems.

The fact that the mononuclear copper meso-tartrate complexes are stronger than their d-tartrate analogues, and the greater basicity of the meso-tartrate(2-) ion can be understood by considering the difference in conformation. The conformation according to Fig. 1, which is the conformation found in crystal structures of meso-tartrate, is the most favourable conformation of a meso-tartrate ion if oxygen-oxygen distances are considered [13]. All other conformations will lead to oxygen-oxygen distances shorter than two van der Waals radii. The adjacent position of the two negatively charged carboxyl groups should, however, imply the presence of greater coulombic repulsions than in the d-tartrate ion with the carboxyl groups in the transoid position. Whatever conformation the free meso-tartrate ion takes in aqueous solution the coordination of a positive ion - in this case Cu²⁺ or H⁺ - and the formation of a complex in which the tartrate ion takes the conformation represented by Fig. 1 will lead to a decrease of repulsive energy. The result will be an increase of the free energy change of the complex formation reaction. When equilibrium constants of reactions that involve an uncoordinated tartrate(2-)

ion are compared (Table 3, reactions no. 1,3 and 6) it turns out that the meso-tartrate constants are about three times greater than the corresponding constants of the d-tartrate system. Then it would be expected that much of the repulsive energy is released and that the difference between the two systems is less when a second ion is coordinated to the remaining carboxyl group. Reactions no. 2, 4 and 5 in Table 3 are examples of such reactions and it appears that the constants of the meso-tartrate reactions are only a factor 1 to 1.5 greater than the corresponding d-tartrate constants.

Although the stability constants of Cu_2T_2 are about the same size in the copper meso- and d-tartrate systems a comparison of the dimerization constants (reaction no. 7 in Table 3) shows that the tendency to form binuclear complexes is much less pronounced in the meso-tartrate system. There are very few reports on binuclear meso-tartrate complexes [2,20,21], which could, of course, be a consequence of the small number of studies on meso-tartrate systems. Among the few binuclear meso-tartrate complexes reported there are two chromium(III) complexes, $\text{Cr}_2\text{T}_2\text{H}_{-2}\text{L}_2$ and $\text{NaCr}_2\text{T}_2\text{H}_{-3}\text{L}_2$ (L = 1,10-phenanthroline or 2,2'-bipyridyl), to which a tartrate-bridged dimeric structure has been attributed for reasons based on spectrophotometric investigations [21]. Tapscott shows in his study of isomer stabilities of tartrate-bridged binuclear complexes [15] that two meso,meso-dimers can certainly be formed without disturbing the conformation or introducing strain in the central carbon-carbon bond of the meso-tartrate ion. The dimers, i.e. the $\Delta\Delta$ - and $\Lambda\Lambda$ -enantiomers,

have to take an octahedral coordination and the asymmetric carbon atoms of the chelate rings at one and the same metal ion must take opposite configurations (Fig. 3). However, in dimers of this kind there are rather short distances either between opposed hydroxyl or between opposed carboxyl groups [15], though an inspection of molecular models makes it seem probable that these distances could be sufficiently increased by a small increase of the angle between the chelate rings without violating the demands of a proper conformation. However, it may also be noted that the carboxyl oxygens are cis-coordinated in these unhydrolysed dimers which is supposed to be unfavourable from an electrostatic point of view. The lower tendency for dimerization observed in the copper meso-tartrate system compared to the d- and dl-systems would be understood against the background of the objections raised against the formation of the meso,meso-tartrate dimers as would the difference between the crystal structures of the copper d- and meso-tartrate trihydrates [8] mentioned in the introduction.

Notwithstanding his statement that the d- and meso-tartaric acids behave completely similar in relation to the copper(II) ion in the formation of various solids, Reihlen [3] presents a copper tartrate with the ratio Cu:T:H equal to 5:4:-6 only in the case of meso-tartaric acid.

The formation of the complex $\text{Cu}_5\text{T}_4\text{H}_{-6}$ may be conceived as the result of a polymerization principle of the same kind as that proposed for the formation of the octanuclear complex $\text{Cu}_8\text{T}_6\text{H}_{-10}$

in the copper d-tartrate system [18,22], i.e. a copper ion joins two tartrate-bridged dimers via two hydroxyl groups at each dimer. In the case of meso-tartrate it may be noted, however, that the meso,meso-dimer turns all the four hydroxyl groups to one side of the dimer and the four carboxyl groups to the other (Fig. 3). Thus, an association of the kind mentioned has to cease when two dimers are joined, i.e. when a complex with five copper and four tartrate ions is formed, provided that the terminal carboxyl groups cannot bring about a further polymerisation.

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Table 1a. Copper meso-tartrate system. Experimental series data.

Series	C_M	C_T^0	C_T^1	C_H^0	C_H^1	E_m^0	E_h^0
nr	/mM	/mM	/mM	/mM	/mM	/mV	/mV
1	1.01	1.00		1.99	-2.96	15.95	528.6
2	2.02	1.99		3.99	-5.97	16.00	528.4
3	5.06	4.98		9.97	-14.82	16.00	528.4
4	10.12	9.97		19.94	-29.7	16.00	528.4
5	20.24	19.94		39.9	-59.7	16.00	528.3
6	2.02	9.97		19.94	-19.81	16.00	528.4
7	5.06	9.97		19.94	-19.97	16.00	528.4
8	2.02	24.9		49.8	-50.2	16.00	528.6
9	5.06	24.9		49.8	-49.5	16.00	528.5
10	10.12	24.9		49.8	-49.0	15.95	528.5
11	20.24	49.8		99.7	-50.1	15.95	528.5
12	1.01	0.00	159.5	0.00	21.4	15.95	528.6
13	2.02	0.00	159.5	0.00	20.6	15.95	528.6

Table 1b. Copper meso-tartrate system. Experimental point data.

v	E _m	E _h	v	E _m	E _h	v	E _m	E _h
/ml	/mV	/mV	/ml	/mV	/mV	/ml	/mV	/mV
Series no 1								
2.00	106.69	722.7	24.00	107.43	759.2	7.00	95.56	712.1
6.00	108.48	748.1	28.00	117.79	772.7	9.00	100.93	724.7
10.00	111.12	771.4	32.00	132.96	793.4	12.00	109.47	741.1
14.00	114.58	781.9	36.00	171.97	854.5	16.00	121.09	757.8
18.00	118.41	790.4	Series no 6			20.00	133.00	773.3
22.00	122.76	799.3	1.00	100.93	682.2	24.00	145.24	789.7
26.00	128.18	809.7	3.00	104.14	698.9	28.00	159.10	809.7
30.00	135.85	823.7	5.00	108.15	714.5	31.00	174.28	833.1
34.00	151.32	850.7	7.00	112.76	729.3	33.00	197.72	870.3
36.00	173.98	887.7	9.00	117.73	743.5	Series no 11		
Series no 2			12.00	125.62	762.1	0.00	71.86	641.1
2.00	98.59	710.4	16.00	137.79	781.9	4.00	79.43	672.6
6.00	101.01	737.3	20.00	152.08	803.3	8.00	87.99	694.8
10.00	104.45	759.3	24.00	175.82	840.5	12.00	96.02	711.8
14.00	108.23	769.4	Series no 7			16.00	103.58	726.0
18.00	112.42	777.7	2.00	89.50	685.8	20.00	110.67	737.6
22.00	117.17	786.4	6.00	94.81	712.5	24.00	117.12	746.8
26.00	123.05	796.7	8.00	97.97	724.4	28.00	123.00	754.5
30.00	131.41	810.9	10.00	101.33	735.3	34.00	130.88	764.5
34.00	148.44	839.5	14.00	108.55	750.7	40.00	137.90	773.4
36.00	177.43	886.8	18.00	116.30	762.2	Series no 12		
Series no 3			22.00	124.82	773.7	0.60	139.44	791.9
2.00	87.74	695.1	26.00	134.16	786.5	1.00	150.38	799.9
6.00	91.30	723.3	30.00	145.00	801.8	1.50	158.35	805.4
10.00	95.64	744.1	36.00	173.69	846.1	2.50	167.50	811.0
13.00	98.89	751.8	Series no 8			4.00	174.85	814.7
16.00	102.28	758.1	1.00	104.39	673.7	6.00	180.73	817.2
20.00	107.27	766.5	3.00	111.49	696.2	10.00	187.76	819.5
24.00	113.19	775.7	5.00	119.50	715.5	16.00	194.02	821.0
28.00	120.85	787.5	7.00	127.63	732.9	24.00	199.08	822.1
32.00	132.58	805.6	9.00	135.26	748.8	32.00	202.23	822.7
36.00	167.84	862.6	12.00	145.10	770.2	40.00	204.46	823.1
Series no 4			16.00	159.42	796.4	Series no 13		
2.00	79.75	683.7	19.00	174.69	821.0	0.60	123.24	774.4
6.00	84.45	713.0	21.00	195.06	854.2	1.00	136.60	784.8
10.00	89.55	733.6	Series no 9			1.50	147.07	793.1
13.00	93.26	741.6	1.00	91.76	660.8	2.50	158.77	802.1
16.00	97.07	748.1	3.00	97.42	690.4	4.00	167.85	808.4
20.00	102.73	756.7	5.00	103.86	708.0	6.00	174.64	812.6
24.00	109.50	766.3	7.00	110.82	723.9	10.00	182.14	816.7
28.00	118.35	778.7	9.00	117.93	738.9	16.00	188.13	819.5
32.00	131.36	797.8	12.00	128.66	758.6	24.00	192.68	821.3
36.00	163.98	854.2	16.00	143.08	780.0	32.00	195.54	822.3
Series no 5			20.00	158.43	802.2	40.00	197.53	823.0
0.00	69.81	652.9	23.00	173.89	825.9	Series no 10		
4.00	74.93	687.8	25.00	195.30	860.6	2.00	83.53	674.1
8.00	81.16	714.8	Series no 10			5.00	90.48	698.3
12.00	87.01	730.1						
16.00	92.86	739.7						
20.00	99.46	748.8						

Table 2. Stability constants of complexes $\text{Cu}_p\text{T}_q\text{H}_r$ formed in acid and neutral copper meso-tartrate solutions calculated from data of potentiometric measurements at 25°C and ionic strength 1.00 M with NaClO_4 as neutral salt. Stated errors are equal to three standard deviations. The percentages state the maximum presence of complexes relative to the total amount of copper in the region used for the calculations.

p q r	β_{pqr}		%
1 1 1	$(1.53 \pm 0.03) \cdot 10^6$	M^{-2}	40
1 1 0	$(1.41 \pm 0.05) \cdot 10^3$	M^{-1}	46
1 2 0	$(2.05 \pm 0.06) \cdot 10^5$	M^{-2}	92
2 2 0	$(3.3 \pm 0.3) \cdot 10^8$	M^{-3}	33
5 4 -5	$(1.09 \pm 0.16) \cdot 10^4$	M^{-3}	22
5 4 -6	1.36 ± 0.08	M^{-2}	91
6 4 -7	$(1.64 \pm 0.13) \cdot 10^{-1}$	M^{-2}	52

Table 3. Equilibrium constants of some corresponding copper d- and meso-tartrate reactions. Constants of the d-tartrate reactions are taken from Ref. 18.

Reaction	K /M ⁻¹ (<u>d</u>)	K /M ⁻¹ (<u>meso</u>)	K _{<u>meso</u>} /K _{<u>d</u>}	no.
$T^{2-} + H^+ \rightleftharpoons HT^-$	$4.90 \cdot 10^3$	$13.3 \cdot 10^3$	2.71	(1)
$HT^- + H^+ \rightleftharpoons H_2T$	$5.57 \cdot 10^2$	$7.59 \cdot 10^2$	1.36	(2)
$Cu^{2+} + T^{2-} \rightleftharpoons CuT$	$4.3 \cdot 10^2$	$14.1 \cdot 10^2$	3.31	(3)
$CuT + H^+ \rightleftharpoons CuTH^+$	$9.0 \cdot 10^2$	$10.9 \cdot 10^2$	1.20	(4)
$HT^- + Cu^{2+} \rightleftharpoons CuTH^+$	$0.78 \cdot 10^2$	$1.15 \cdot 10^2$	1.47	(5)
$CuT + T^{2-} \rightleftharpoons CuT_2^{2-}$	$0.57 \cdot 10^2$	$1.45 \cdot 10^2$	2.54	(6)
$2 CuT \rightleftharpoons Cu_2T_2$	$2.20 \cdot 10^3$	$0.16 \cdot 10^3$	0.08	(7)

Fig. 1. Conformation of meso-tartrate groups found in the solid state.

Fig. 2. Emfs versus C_H/C_M , $C_M = C_T = 10$ mM. Full lines represent values of the copper meso-tartrate system calculated from the stability constants of Table 2. Dashed lines represent the copper d-tartrate system and are calculated from stability constants taken from Ref. 18.

Fig. 3. Sketch of a tartrate-bridged meso,meso-dimer with an idealized octahedral geometry.

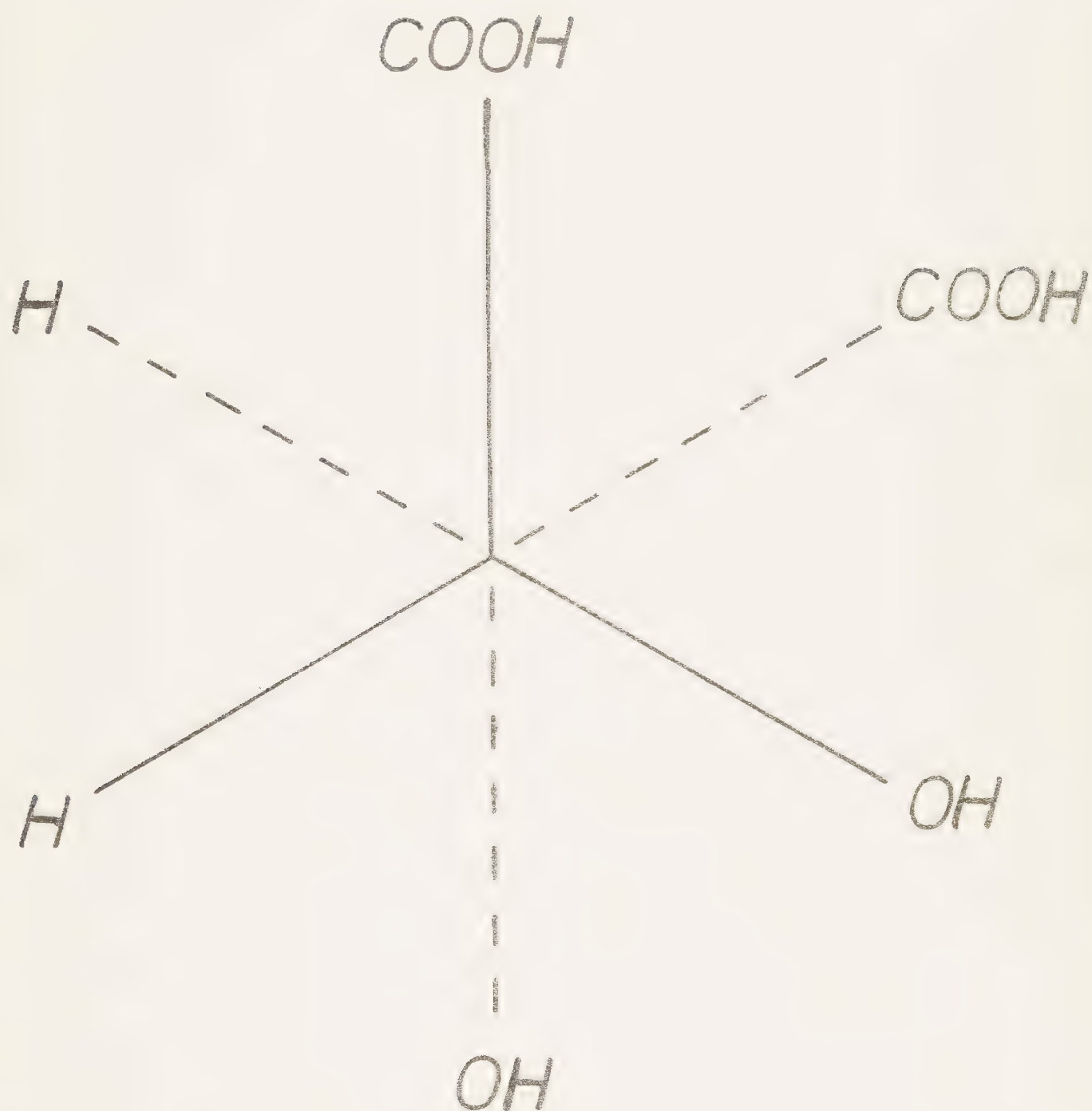


Fig. 1

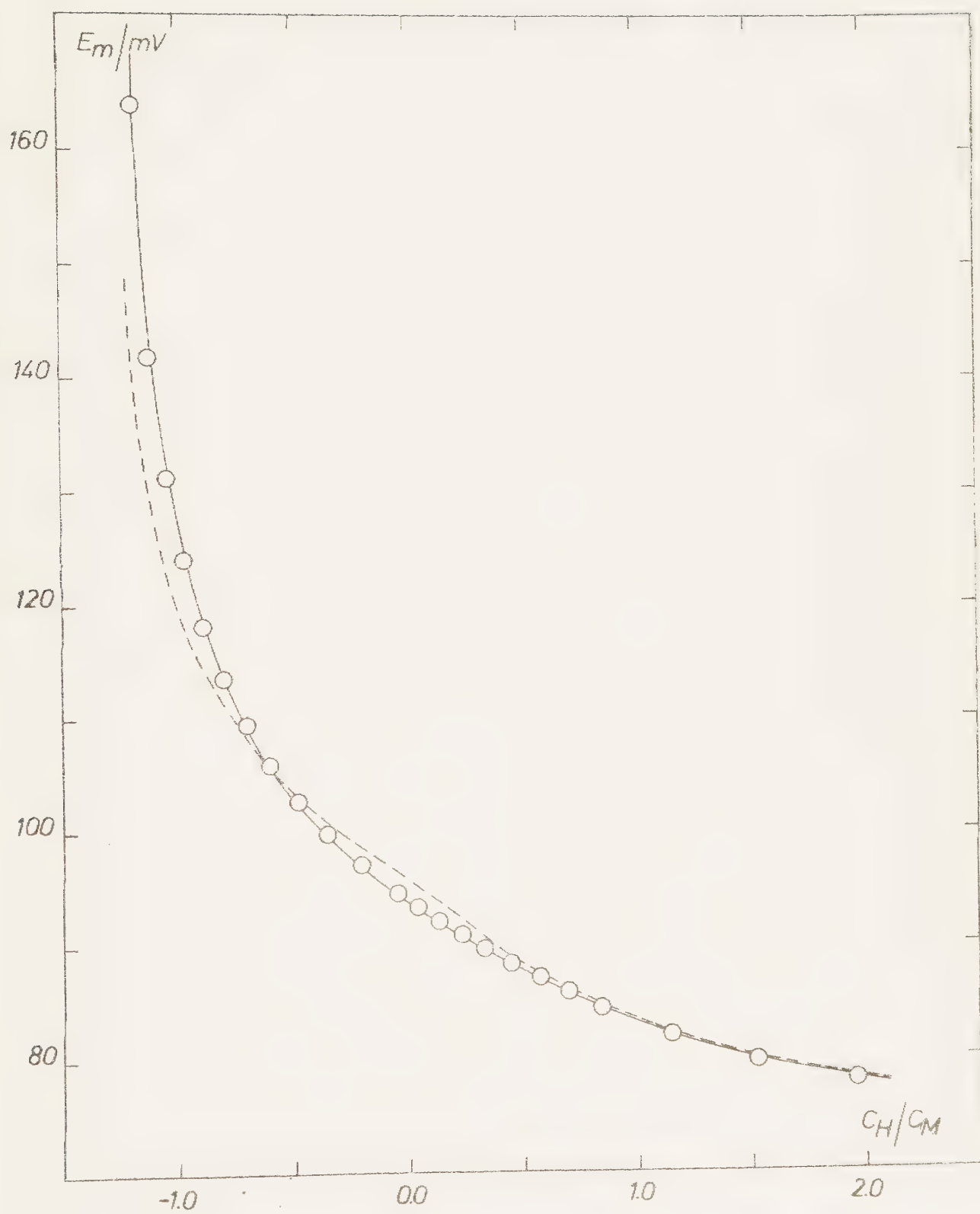


Fig. 2a



Fig. 2b

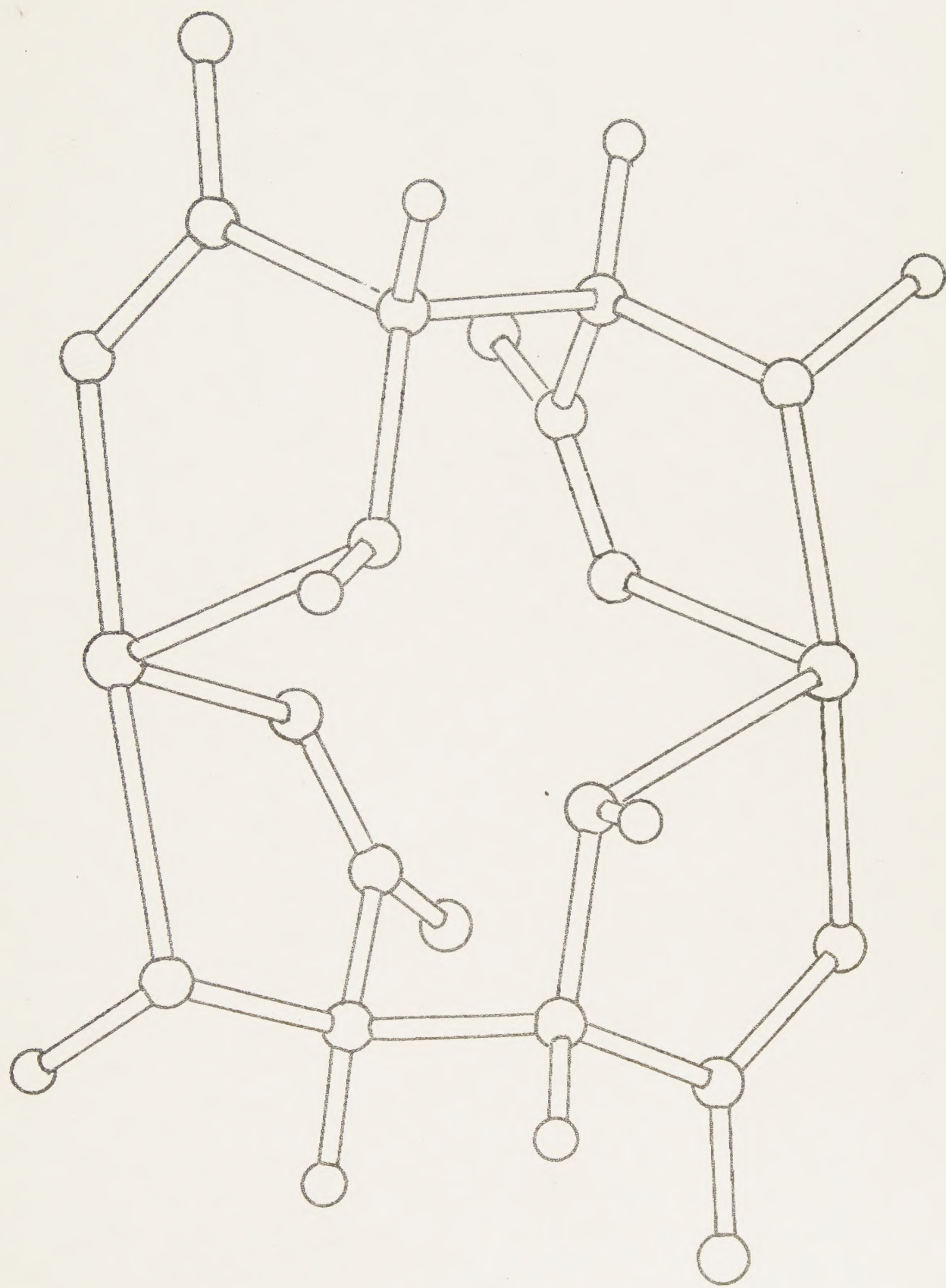


Fig. 3

